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Microwave Ultrasonics

High-frequency elastic waves reveal structural and dynamical properties of condensed matter.

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Microwave ultrasonics refers to the study of elastic wave propagation in solids and liquids at microwave frequencies—that is, frequencies in the range of roughly 10^9 to 10^{11} cycles per second. Until a few years ago elastic wave studies were limited to frequencies below about 10^9 cycles per second, but since that time the earlier methods have been extended and new ones have been developed for converting electromagnetic energy into sound at the higher frequencies (*1–4*). What do such studies tell us?

It is instructive to consider first the character of elastic wave motion in an idealized crystalline solid (*5*). As envisioned on the microscopic scale, we have a periodic array of atoms joined together by electronic forces. For our purposes we may view the atoms as point masses connected by ideal springs. A simple analysis (*6*) of this model yields a dispersion relation between frequency ν and reciprocal wavelength k $(= 1/\lambda)$ of the sort given in Fig. 1. In Fig. 1 there are three dispersion curves, one for the longitudinal (compressional) wave and the other two for transverse (shear) waves. Pure longitudinal and transverse waves are possible only for waves propagating along crystal axes of high symmetry. Also, if the smallest crystalline unit cell contains more than one atom, additional branches, called optical branches, will lie above the curves of Fig. 1. But we need not concern ourselves with these details here. The thing to note is that the frequency extends from zero to, typically, 10^{13} cycles per second and the wavelength λ ranges from dimensions of a macroscopic sample down to a few angstrom units—the interatomic spacing and, incidentally, a typical x-ray wavelength. Further, it turns out that the slope of the curves, $\partial\nu/\partial k$, at low frequencies is high and is a direct measure of the velocity determined by the bulk elastic constants, whereas at very high frequencies the slope decreases and is a direct measure of the interatomic forces. That the slope (velocity) decreases at higher frequencies results from the shorter elastic waves' being able to "see" the discontinuous microstructure of the crystal, which is invisible to long waves. Discernible bending of the curves appears at a frequency of about 10^{12} cycles per second and a corresponding wavelength λ of some 30 atomic spacings.

The main features of Fig. 1 have been verified by x-ray and neutron diffraction studies on a number of single crystals (*7*). (X-rays reveal the elastic wave spectrum by revealing its influence on the atomic spacing; in the neutron diffraction studies the same information is given by the energy shift of the scattered beam.) Nonetheless, an important feature is left out of our model. This missing feature is the scattering and attenuation (and often additional dispersion) produced by various dynamical interactions with the sound wave. In a real crystal such interactions typically arise from anharmonic forces between atoms, the presence of free charge carriers, coupling to localized spin states, and the presence of impurities. Let us briefly examine these in turn.

1) The electronic binding forces between atoms are not quite ideal springs. Hence, the restoring forces are proportional not only to the first power of the displacement but to higher powers of the displacement as well. This nonlinearity (anharmonicity) means that an elastic wave of any one frequency, once excited, will be attenuated as the result of conversion of its energy into waves of other frequencies. In other words, the elastic waves as we picture them are not pure eigenstates of the crystal; if they were, their lifetimes would be very long, even infinite. This damping out becomes more severe as we go to higher frequencies because the number of elastic waves per unit frequency interval and the rate of energy transfer increase rapidly with frequency.

2) In metals and semiconductors the charge carriers (electrons and holes) interact with elastic waves in numerous ways, hence increase the attenuation. This electron-phonon interaction not only attenuates elastic waves but also produces such diverse phenomena as electrical resistance and electrical superconductivity (the state in which there is perfect diamagnetism and zero resistivity).

3) Spin-phonon interactions can likewise extract energy from an exciting elastic wave. This effect is most pronounced for paramagnetic ions in a dielectric crystal. In this case changes in the crystalline electric field produced by the elastic wave are coupled to the unpaired electron spin of the ion by the electron spin-orbit coupling. When the energy, $h\nu$, of an elastic wave quantum (or phonon) equals the energy difference between the spin levels, resonant paramagnetic transi-

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tions will occur, with subsequent loss of acoustic energy. It often happens, because of the difference in coupling, that more paramagnetic transitions are possible with elastic waves than with electromagnetic waves. Hence, acoustical paramagnetic resonance can sometimes produce transitions not seen in the more familiar electromagnetic resonance experiments.

4) Another type of resonant absorption can occur as a result of the presence of impurity molecules (mostly in dielectrics) and is of particular importance in thermal energy transport. To date such effects have been observed mainly in thermal conductivity experiments in which the elastic wave frequencies are several hundred thousand or more megacycles. Such molecular-impurity resonances are complicated and often involve tunneling or localized vibrational and rotational modes of the impurity.

Other loss mechanisms also exist, but in the interest of brevity I do not discuss them here. I might note, however, that any of these processes, if thoroughly understood, would tell us a lot about the dynamical properties of solids and liquids. Moreover, it happens that these processes often occur at elastic wave frequencies above 10^9 cycles per second. Hence, in order to study these phenomena directly, it would be advantageous to have monochromatic-elastic-wave sources and detectors with which to measure scattering, dispersion, and attenuation at very high frequencies. A start in this direction has been made by the recent perfection of techniques in microwave ultrasonics.

Generation and Detection of Very-High-Frequency Elastic Waves

To date, the easiest and most direct method of generating and detecting high-frequency elastic waves is still the piezoelectric-transducer technique, the tried and true method of low-frequency ultrasonics. There are, indeed, other methods, and I discuss some of these presently. But the piezoelectric transducer is the simplest, it can accommodate the complete spectrum of elastic wave frequencies, and its theory of operation has wide generality.

If brief, a piezoelectric crystal (for example, quartz) will develop a net electrical polarization if it is placed under elastic strain along certain crystallographic directions. Conversely, such a crystal will suffer an elastic strain if it is placed in an electric field. If, now, the electric field varies sinusoidally with time, a strain field with the same time variation is produced at the free surfaces of the crystal and propagates to the interior. Analysis (*8*) shows that, for an electric field varying harmonically with time, electrical energy is converted to ultrasonic energy over a distance from each free surface equal to half a sonic wavelength. This situation holds for all frequencies; it is illustrated in Fig. 2. The velocity of sound in a solid is, typically, some 5×10^5 centimeters per second. Hence, at low frequencies a sonic half-wavelength will often be comparable to dimensions of the sample, whereas at microwave frequencies —say, 10^{10} cycles per second—the wavelength will be some 5000 angstroms, an optical wavelength. This state of affairs has led several authors to look upon low-frequency excitation as a bulk effect and upon high-frequency excitation as a surface effect. Such descriptions can be misleading because they suggest that something different is happening in the two cases, whereas in fact the excitation process is the same for all frequencies. Why, then, is it difficult to generate very-high-frequency elastic waves? Or is it really?

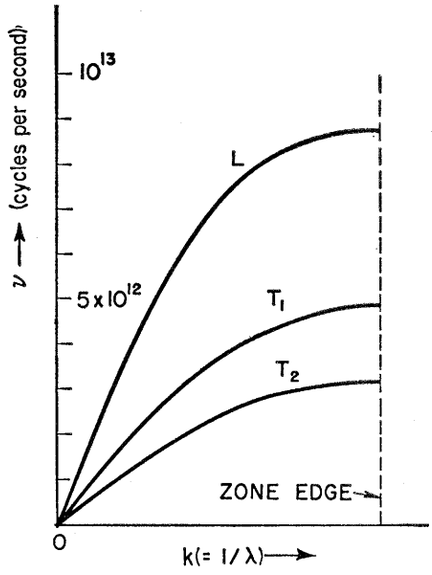

Fig. 1. Typical dispersion curves for longitudinal (L) and transverse (T) elastic waves along a symmetry axis of a crystal containing one atom per unit cell; it is assumed that there is no wave attenuation. Real crystals have various loss mechanisms (see text) which produce scattering, attenuation, and additional dispersion.

Apart from the matter of attenuation, which we come to later, there is no difficulty *in principle* in exciting elastic waves of any frequency by means of an electrical mechanical transducer. There arise, however, two practical problems. The first is that of achieving sufficient electromagnetic energy at the desired frequency. The second is that of impedance matching between the exciting electromagnetic wave and the piezoelectric crystal, the object of which is to insure that a useful fraction of electromagnetic energy is converted to sonic energy. These problems are, of course, related.

Regarding the matter of power, there exist pulsed magnetrons that yield 1 kilowatt at frequencies up to about 80,000 Mc/sec—a power output which is ample. Carcinotrons and klystrons exist which produce useful power outputs of the order of watts and tens of milliwatts, respectively, at frequencies from 80,000 to 150,000 Mc/sec. For typical piezoelectric crystals (for example, quartz, cadmium sulfide, zinc sulfide, zinc oxide), a calculation (*8*) shows that between 10^{-2} and 10^{-4} of the exciting electromagnetic energy can be converted to sound. Thus, with present microwave technology, 10 milliwatts of radio-frequency driving energy is sufficient if the ultrasonic attenuation is low enough, as it probably is in the case of crystals of high perfection. For still higher frequencies (roughly 10^{11} to 10^{13} cycles per second), only a few electromagnetic sources exist. These sources are lasers operating at a few discrete frequencies corresponding to certain molecular transitions (*9*). Power outputs of the order of watts have been achieved in some cases. For these frequencies electromagnetic wave sources are still mainly laboratory devices, but it seems reasonable to expect that they will soon be sufficiently refined to provide a practical means of generating elastic waves by transducer action at thermal phonon frequencies.

Even if we assume that sufficient electromagnetic power is available over the complete elastic wave spectrum, we are still faced with the problem of impedance matching between the exciting electromagnetic wave and the transducer. The crux of this problem is outlined in Fig. 3, wherein a series of electrically resonant circuits and approximate frequency ranges are shown schematically. The resonant cavity is simply a means of providing the largest

possible electric field at the surfaces of the piezoelectric crystal for a given input of radio-frequency power to the cavity. Hence, the cavity acts as a step-up transformer, the effective-turns ratio being determined by the electrical Q (Q is the "quality factor" or sharpness of resonance). For any given value of piezoelectric conversion constant, *all* the incident electromagnetic energy could be converted to sonic energy provided the Q were sufficiently high (*10*). At the higher frequencies high Q's are harder to achieve; moreover, the resonator dimensions become small, and it is therefore necessary to operate the cavity in a high electrical mode if crystals of convenient size are to be accommodated. Nonetheless, it appears feasible to build cavities of suitable size and Q to achieve significant production of even thermal-frequency phonons if appropriate electromagnetic sources become available.

If we succeed in generating such waves, we must devise some means of detecting them. One way, of course, would be to use the piezoelectric effect in reverse. Theory shows that a plane elastic wave incident normal to a smooth piezoelectric surface will produce a surface polarization that varies with time. If the piezoelectric crystal is placed in a resonant cavity, a detectable portion of electromagnetic energy will flow away from the crystal. At frequencies up to roughly 10^{11} cycles per second, such radiation is easily detected by means of a microwave superheterodyne receiver. At frequencies much above this, the superheterodyne scheme becomes impractical with present microwave technology, and other methods, involving direct quantum detection, appear more suitable.

In addition, it should be noted that piezoelectric detection of very-high-frequency elastic waves is itself rendered difficult by the shortness of sonic wavelength—a problem entirely separate from that of developing a suitable microwave receiver. Obviously, maximum sensitivity will be achieved only if the piezoelectric polarization has the same phase over the entire surface of the crystal. Realization of this condition requires very precise geometry: the surface must be flat, and the wave must strike the surface at normal incidence to within an angle of the order of λ/D, where D is the average diameter of the crystal. Moreover, even if this condition is met (a difficult feat above, say, 10^{11} cycles per second), it is imperative that the wave surfaces not be distorted in shape as the waves traverse the crystal (*11*). Unfortunately, various naturally occurring inhomogeneities make this state of affairs unlikely at high frequencies. Hence, to summarize: the piezoelectric transducer will generate sound at any frequency provided electromagnetic energy and suitable cavities are available, but, as regards detection, the piezoelectric method is severely limited by geometrical effects at short wavelengths. Moreover, even if this were not the case, we still lack sensitive microwave receivers for frequencies above a few hundred thousand megacycles.

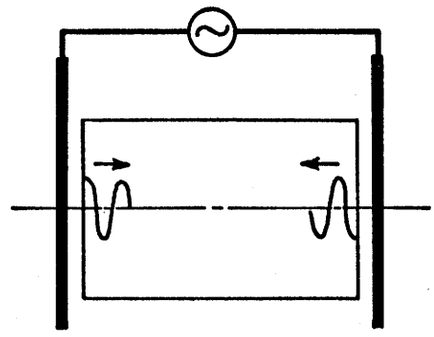

Fig. 2. The initiation of a sinusoidally varying elastic wave at the surfaces of a piezoelectric crystal (see *8*).

Before considering a basically different method of high-frequency sound production and detection, I should call attention to the existence of magnetoelastic transducers—for example, ferromagnetic films which are driven by the *magnetic* component of the incident electromagnetic wave, as demonstrated by Bommel and Dransfeld (*12*) and Pomerantz (*13*). The magnetoelastic transducer is analogous to the piezoelectric transducer, the magnetic field H replacing the electric field E; hence, the two problems are basically the same. Until quite recently ferromagnetic film offered the special advantage that it could be applied to a surface by evaporation, with the result that the bond between transducer and sample was nearly perfect. However, in 1964 J. de Klerk of the Westinghouse Laboratories developed a method whereby thin films of the piezoelectric crystals zinc sulfide and cadmium sulfide can be evaporated onto a wide variety of substances (*14*). This procedure, in contrast to the older methods, likewise yields an excellent bond between transducer and sample and so places the piezoelectric transducer in a very competitive position. A typical pulse-echo apparatus for generating and detecting elastic waves piezoelectrically at microwave frequencies is shown schematically in Fig. 4.

So far I have discussed the use of an electromechanical transducer, of which magnetoelectric and piezoelectric transducers are common examples. Under typical conditions such a transducer is *linear*—that is, it converts electromagnetic waves of one frequency to elastic waves of the same frequency, and vice versa. However, it is also possible to generate sound by *nonlinear* processes involving intense electromagnetic excitation. An example of a nonlinear process is the coupling of light waves to sound waves through electrostriction—the compression or expansion of materials by means of electric fields in the light wave. Such in-

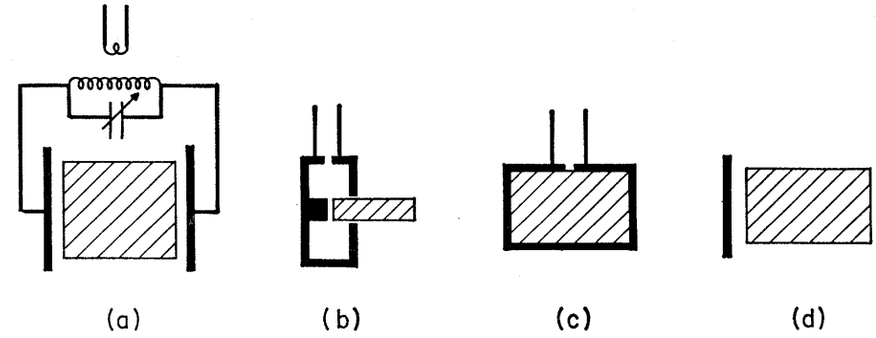

Fig. 3. Resonant-cavity configurations and suggested frequency ranges: (*a*) conventional tank circuit, operation up to 100 Mc/sec; (*b*) reentrant cavity, operation up to 50,000 Mc/sec; (*c*) TE (transverse electric) or TM (transverse magnetic) enclosed, operation between 10,000 and 500,000 Mc/sec; (*d*) hybrid end-plate reflector cavity of the type common to most lasers, operation above 500,000 Mc/sec. The function of a resonant cavity is to provide maximum electric field, at the piezoelectric surface, per watt of available electromagnetic excitation.

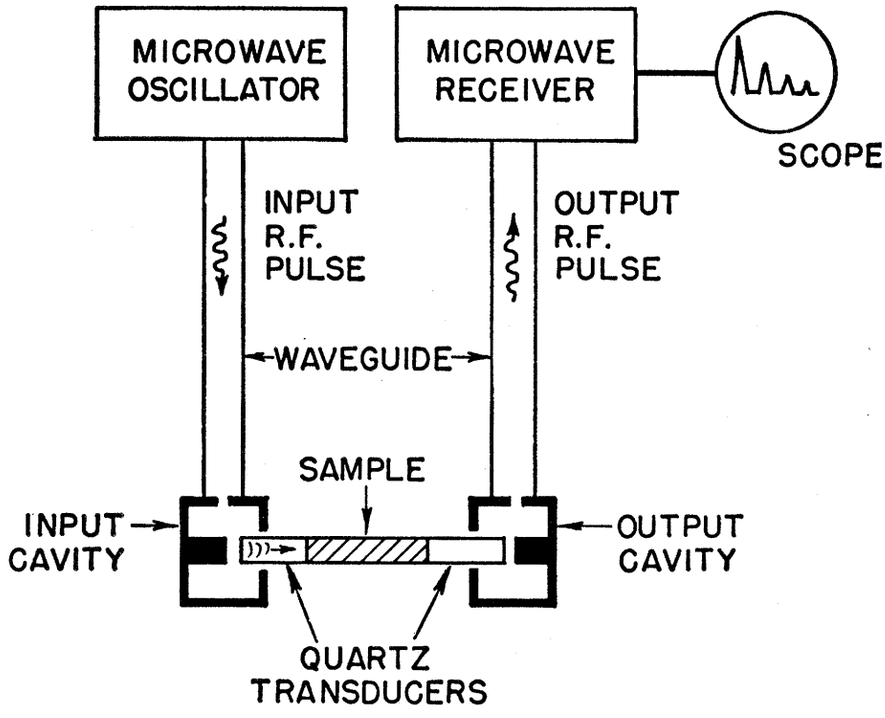

Fig. 4. Schematic diagram of a typical pulse-echo ultrasonic apparatus. Single-ended operation can be achieved by removing one cavity and connecting the receiver to a directional coupler inserted in the remaining waveguide (*55*).

teraction is known as stimulated Brillouin scattering.

Townes and his collaborators have analyzed this process at length and show (*15*) that the internal electrostrictive pressure is very nearly proportional to E^2 for most solids and liquids. It turns out that, for an electromagnetic energy flux of some 300×10^6 watt/cm^2, the pressure is of the order of 10^5 dyne/cm^2. Such intense beams of energy can be obtained with pulsed ruby lasers, with the result that very intense sound waves can be produced by this method.

To see how this happens, consider a medium irradiated by two beams of light at slightly different frequencies ν_1 and ν_2 ($\nu_1 > \nu_2$). Since the pressure is proportional to E^2, the medium will be compressed and expanded at the beat frequency ($\nu_1 - \nu_2$) of the two beams. Analysis shows that, beyond a certain threshold of excitation and under certain conditions, acoustic waves of high intensity will build up at the beat frequency (*16*). These conditions are as follows:

$$h\nu_{\text{sound}} = h\nu_1 - h\nu_2 \text{ (energy conservation)} \quad (1)$$

$$\mathbf{k}_{\text{sound}} = \mathbf{k}_1 - \mathbf{k}_2 \text{ (phase matching)} \quad (2)$$

where $\mathbf{k}_{\text{sound}}$, $\mathbf{k}_1$, and $\mathbf{k}_2$ are the wave number vectors for the sound wave and the two light waves, respectively. (A wave number vector is parallel to the direction of wave propagation and has a magnitude equal to the reciprocal of the wavelength.) From condition 2 the frequency of the sound wave is found to be

$$\nu_{\text{sound}} = \frac{2v}{c}\nu_1 \sin\left(\frac{\theta}{2}\right) \quad (3)$$

where v is the sound velocity in the medium, c is the velocity of light, and θ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. The ratio (v/c) for most materials is such that the sound frequency can be as high as 10^{11} cycles per second, and even 10^{12} cycles per second in some cases of large v. If E_1, the higher-frequency light wave, is of large amplitude, and if its amplitude is larger than that of E_2, the second light wave, both the sound wave and E_2 will be amplified at the expense of E_1. In contrast to the situation for the electromechanical transducer, the condition of phase matching (condition 2) means that for nonlinear electromagnetic excitation the sound keeps in step with the electrical driving fields and so amplification occurs over a huge number of sonic wavelengths. This process is equivalent to Bragg reflection of the light wave E_1 by a moving grating of periodic density, which is the sound wave. Because the grating moves, the reflected light wave E_2 is Doppler-shifted either up or down by an amount equal to the frequency of the sound wave. Upward shift occurs if the sound wave moves toward the light beams, downward shift occurs if the motion is away from the light beams. Figure 5 depicts this behavior, all of which is implied by Eqs. 1, 2, and 3. Recent experiments (*15*) have amply demonstrated these relationships. This method of sound generation has the advantage of producing phonon beams of an intensity ($\sim 10^3$ watt/cm^2) that greatly exceeds the capabilities of present electromechanical transducers, and thus may be particularly relevant to studies in which liquids are used. The method suffers at present from a disadvantage: the amplitude, polarization, and direction of propagation of the sound produced are more difficult to control than in the case of the electromechanical transducer. These limitations pertain to practice rather than principle and so may be removed with further refinements of experimental technique.

Is detection of high-frequency sound also possible with the above-mentioned nonlinear process? Yes, but somewhat indirectly. One can *deduce* the presence of an elastic wave by observing the emerging light wave E_2. Equations 1, 2, and 3 then give the frequency and direction of the elastic wave, once ν_1, ν_2, and θ are determined. Moreover, the *amplitude* of sound can be calculated, by a more refined analysis, if E_1 and E_2 and the properties of the medium are known. This method of detection was first analyzed by Brillouin long ago in connection with light scattering by elastic waves at kilomegacycle frequencies in transparent media. It is also the basis for detecting sound above 10^{12} cycles per second with x-rays and thermal neutrons (de Broglie waves) (*7*, *17*) (see Fig. 5).

Present Status of Ultrasonic Research

To date, in most of the research with high-frequency sound, frequencies no higher than about 10^{10} cycles per second have been used, primarily because of present limits in experimental technique. In this frequency range there were two problems of particular interest in the early experiments. I consider these next, since they illustrate principles characteristic of many phonon interactions.

The first problem concerns phonon-phonon scattering, or the interaction of sound with itself which is caused by the anharmonic forces between atoms in nonmetallic crystals. The occurrence of this scattering raises the question, How does the attenuation of an ultrasonic beam change with frequency, and with sample temperature? Because of the vast number of elastic waves present in any sample at a finite temperature, it is difficult to predict such behavior from theory. Early treatments of losses in dielectric crystals showed that the attenuation increased with frequency and temperature, but the quantitative details were not clear. Many people felt intuitively that a sound wave at, say, 10,000 Mcy/sec (10^{10} cycles per second) would have a very short lifetime, if, indeed, it could even be generated. Hence it came as a surprise to find that even a crystal of high perfection, such as quartz, could transmit a sound wave of microwave frequency over distances of from 100 to thousands of centimeters at temperatures in the helium range (4°K) and even higher (*3*, *18*).

Figure 6 presents the results of a number of investigations of compressional waves ranging in frequency from 10^9 to 7×10^{10} cycles per second. At a temperature of a few degrees Kelvin the attenuation appears to reach zero, whereas in fact it is still finite, though so small as to be difficult to measure. In some crystals of quartz the minimum attenuation is less than 1/50 decibel per centimeter (db/cm) at 10^{10} cycles per second.

Mathematical description of the curves of Fig. 5 is a complicated matter which I do not take up here. Nonetheless, the basic reason why attenuation occurs at all, and why it increases with temperature, can be stated simply. The forces between atoms are nonlinear, so a sound wave of one frequency can mix with itself or with a wave of another frequency and produce "sum" and "difference" frequencies. This mixing or beating of waves extracts energy from the incident (driving) wave, thereby causing attenuation. The equations for such an interaction are

$$h\nu_1 + h\nu_2 = h\nu_3 \quad (4)$$

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 \quad (5)$$

and since the process involves three frequencies, it is called a "three phonon" process. (Similarly, a "four phonon" process can occur, but it is less usual.) The transition probability for these processes is not given by Eqs. 4 and 5 but is determined through a more detailed analysis. The theoretical results show that the transition probability for such a process is proportional to the strength of the nonlinear forces between atoms, to the amplitude of the other waves present, and to the amplitude of the incident driving wave. Since, at higher temperatures, more elastic waves are present in states of higher excitation, we should expect the attenuation to rise with temperature. These ideas were originally put forward by the Russian scientist A. I. Akhiezer (*19*) and by Landau and Rumer (*20*) long before it became possible to conduct experiments at microwave frequencies. More recently, Woodruff and Ehrenreich (*21*) have extended and refined the theory, and their results fit closely the data of Fig. 6.

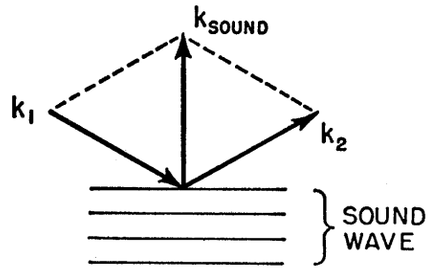

Fig. 5. Diagram showing how intense light wave $\mathbf{k}_1$ builds up sound wave $\mathbf{k}_s$ and reflected light wave $\mathbf{k}_2$ when conditions 1 and 2 of the text are satisfied. $|\mathbf{k}_1| \cong |\mathbf{k}_2|$.

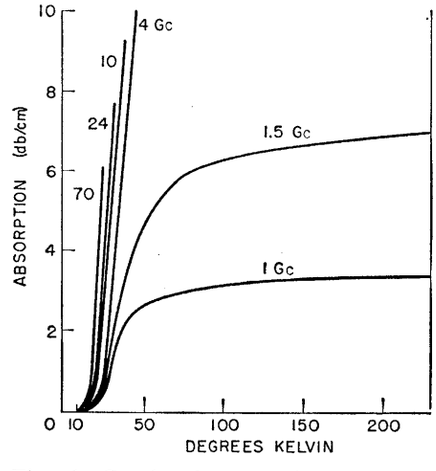

Fig. 6. Graph of attenuation of longitudinal waves versus temperature, in quartz. Other dielectrics behave in a qualitatively similar way (1 Gc = 10^9 cycles). [Based on data from Bommel and Dransfeld (*2*), Thaxter and Tannewald (*4*), and Jacobsen (*18*)]

Recent experiments by Dransfeld and his collaborators (*22*) and by Pomerantz (*23*) on several insulating crystals have provided the most complete picture to date of elastic wave attenuation at high frequencies. The main observation to emerge from such experiments is that the attenuation curves flatten out at higher temperatures and approach a limiting value (which, for longitudinal waves, is proportional to the square of the frequency). At the lowest temperatures all curves approach a very low, but finite, value of attenuation which is nearly independent of temperature. The curve at 70,000 Mcy/sec exhibits some fine structure at the low end, caused by, presumably, defects of one kind or another in the crystal (*4*). Although the data of Fig. 6 apply to longitudinal waves, rather similar results obtain for transverse waves as well. It will be very interesting to examine the change of attenuation with change in temperature at much higher frequencies, as such measurements will reveal details of crystal perfection and the interatomic force field.

The second problem of interest concerns the coupling between the electron spin states of ions and the phonon field of the crystal, often referred to as spin-phonon interaction. Earlier work on paramagnetic relaxation raised the question of how spins and elastic waves exchange energy. Hence, when it became practical to generate elastic waves of frequencies corresponding to those at which spin transitions typically occur (that is, microwave frequencies), this question received immediate attention (*24*).

A particularly good example of the spin-phonon problem is provided by the work of N. S. Shiren (*25*) on the divalent ferrous ion Fe^{++}, which occurs as an impurity in the dielectric crystal magnesium oxide (MgO). In this case the ion has an effective spin of 1, which, under the action of a magnetic field (direct-current), yields three spin states. Moreover, because the coupling between the spins and the phonon field is very strong, the spins drastically influence elastic-wave propagation.

Specifically, when the elastic-wave frequency approaches the frequency of an allowed spin transition, the wave suffers strong attenuation and dispersion (modification of wave velocity), a situation which parallels closely the dispersion and absorption

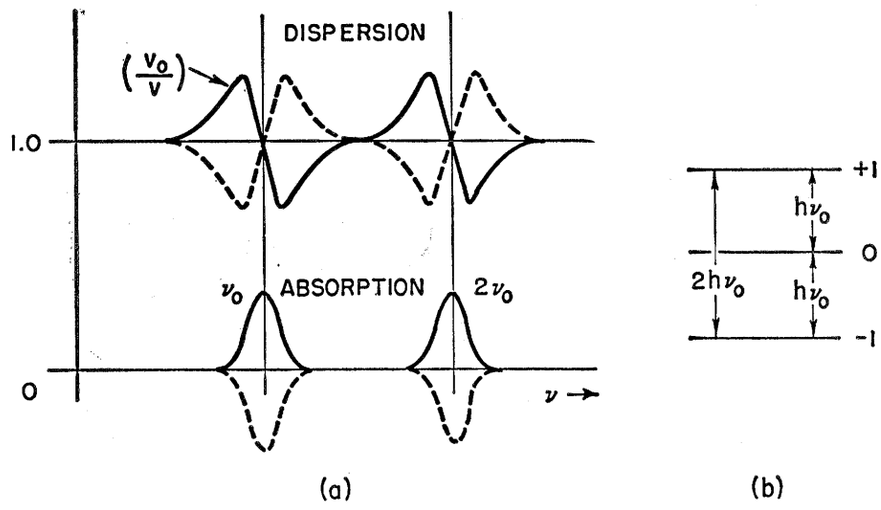

Fig. 7. (*a* and *b*) Ultrasonic dispersion curves and energy levels, respectively, of the paramagnetic ion Fe^{++} in the host lattice of magnesium oxide.

of light by resonant electronic states of atoms. It is significant that, in the case of Fe^{++} (and of other members of the ion group), the coupling of sound waves to spins is stronger and of a different type than the coupling of *electromagnetic* waves to spins. This has two consequences. First, it is often easier to observe such resonances by means of sound waves than by means of electromagnetic waves. Second, transitions which are forbidden to electromagnetic waves may be allowed to ultrasonic waves. For Fe^{++} in MgO, transitions between the spin states $S_z = \pm 1$ are forbidden to photons but allowed to phonons. Hence, in some cases, ultrasonic resonance gives information additional to that obtained from the more conventional electromagnetic resonance. It also happens that the ultrasonic method gives directly the coupling factor between spins and crystal lattice—information which can be obtained from conventional electromagnetic resonance indirectly, through application of static strains to the crystal. Additional studies of spin-phonon interactions have been made by Tucker (*26*), Dobrov (*27*), Rowell (*28*), Hemphill (*29*), Donoho (*30*), Bolef (*31*), Orbach (*32*), and others (*33*). The closely related problem of the influence of paramagnetic impurities on thermal conductivity has been experimentally investigated by Morton and Rosenberg (*34*) and analyzed by Orbach (*35*).

Stimulated by Shiren's work on Fe^{++}, K. W. H. Stevens and I developed a first-order theory of the ultrasonic dispersion produced by such spin-phonon interaction (*36*). We proposed that wave motion within a paramagnetic medium comprises a mixture of sound wave and spin wave, these two waves being coupled and moving synchronously through the crystal. At frequencies close to resonance, the spin-wave component can be very large, thus such composite wave propagation is quite different in nature from pure elastic wave motion. Hence it is not surprising that, near resonance, the wave velocity differs from that of a pure elastic wave, the elastic wave velocity obtaining only at frequencies far from resonance or in the absence of spins. A similar phenomenon occurs for light waves propagating through, say, a gas of resonant atoms. In this case the total wave field is a composite of the normal electromagnetic field and an atomic polarization field, the latter becoming large at frequencies close to resonance. These ideas are summarized in Fig. 7 for the ultrasonic case; a normal spin population (that is, a population in which most of the spins are in the lower energy states) is assumed. These early results have been extended and incorporated in a recent and more comprehensive description of spin-lattice relaxation, by Giordmaine and Nash (*37*), and studied experimentally by Guermeur *et al.* with the aid of an ultrasonic interferometer (*38*).

Besides ultrasonic dispersion of the simple kind just discussed for longitudinal waves, there may occur a rotary dispersion for transverse waves (*39*). Here the plane of transverse vibration is rotated as it moves through the spin system, just as the plane of polarized light rotates during traversal of certain optically active media (the Faraday effect). A striking example of this phenomenon was theoretically predicted by Kittel (*40*) and demonstrated experimentally by Matthews and LaCraw (*41*) for transverse sound waves moving through a ferromagnetic spin system.

Returning to the simple case of nonrotary dispersion, one naturally asks what happens when, say, more spins are in state +1 than in states 0 or −1. No one familiar with the maser principle will be surprised to learn that elastic waves traversing an inverted spin system at a resonance frequency are amplified rather than attenuated —that the spins emit phonons coherently and so build up the passing wave. In fact, if the condition of inversion is maintained, the elastic wave field will build up into a steady-state oscillation, in the same way that an optical wave field builds up in a laser. Moreover, an inverted population will also invert the dispersion (v_0/v)—that is, the phase velocity v will now be larger than v_0, where v_0 is the sound velocity in the limit of zero spin-phonon coupling. However, according to theory, this state of affairs should not produce *signal* velocities exceeding v_0, contrary to what a casual glance at the dispersion curve suggests (*42*).

Phonon amplification by stimulated emission has been demonstrated by E. B. Tucker (*43, 44*) for the chromium ions Cr^{3+} in ruby and by N. S. Shiren (*45*) for Fe^{++} and Ni^{++} in MgO. The Fe^{++} and Ni^{++} studies required spin inversion by pulses of radio frequencies ("fast passage"), owing to the symmetrical energy level spacings and the strong coupling to lattice, whereas the chromium can be maintained in an inverted state continuously. Power amplification of the order of 1 decibel and 10 decibels per centimeter has been obtained for Cr^{3+} and Fe^{++}, respectively. A slightly different type of ultrasonic amplification by stimulated emission from the translational kinetic-energy states of charge carriers in semiconductors has been demonstrated by Hutson, McFee, and White (*46*) and by Pomerantz (*47*). At the moment it appears that the phonon maser will be of greatest

usefulness as a low-noise amplifier of sound, although its potential for this use is yet to be exploited.

Two additional interesting possibilities emerge from studies of the strong spin-phonon coupling of Fe^{++}, and these have been investigated by Shiren. They are parametric amplification (*21, 48*) and incoherent detection (*49*) of sound.

In the parametric amplification experiment, elastic waves of different frequencies were mixed by the nonlinear (anharmonic) forces between atoms in a crystal of magnesium oxide. Suppose two longitudinal waves of frequency ν_p and ν_s, respectively, are propagated through the crystal simultaneously, and that $\nu_p > \nu_s$. The wave of frequency ν_p is the "pump" wave; that of frequency ν_s, the "signal" wave. Normally, the anharmonic forces will produce additional waves at frequencies $(\nu_p + \nu_s)$—and also waves of higher frequencies, which we can neglect here. Under certain conditions it is possible to achieve significant amplification of the signal wave ν_s. The conditions are (i) that the amplitude of the pump wave be sufficiently large, and (ii) that formation of a wave of sum frequency $(\nu_p + \nu_s)$ be prevented. What Shiren did was to suppress generation of the wave of sum frequency by destroying the phase-matching condition (Eq. 5) by means of the $\Delta m = 2$ transition Fe^{++}. (By $\Delta m = 2$, I refer to a spin transition in which the spin projection along the magnetic field changes by two units—that is, from the state $S_z = -1$ to the state $S_z = +1$.) Under this condition energy from the pump flows into both the "idler" wave $(\nu_p - \nu_s)$ and the signal wave ν_s. If the amplitude and frequency of the signal wave exceed those of the idler wave, then amplification at ν_s will be favored (*50*).

Shiren also demonstrated that the up-conversion process—that is, the process by which a wave of frequency $(\nu_p + \nu_s)$ is generated—proceeds very rapidly and efficiently unless the phase-matching condition is destroyed at this frequency. In fact, signal-power conversions of some 70 percent were observed, with pump and signal frequencies in the neighborhood of 10,000 Mc/sec but differing by as much as 1000 Mc/sec. This observation suggests that it may be practical to generate waves in the range of a few hundred thousand megacycles by this nonlinear process, since a kilowatt or so of power is available from magnetrons operating near 80,000 Mc/sec.

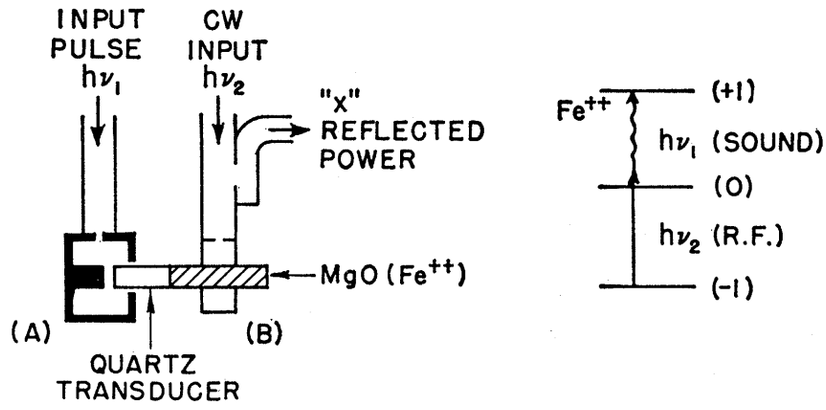

Fig. 8. Schematic representation of Shiren's method of incoherent detection of ultrasonic energy by means of double quantum transition of Fe^{++} (see text).

In the experiment on incoherent detection of sound, a double quantum transition is employed, involving quanta of sound energy and electromagnetic energy. The experiment is shown schematically in Fig. 8. Here the troublesome matter of phase coherence at short wavelengths is eliminated by detecting sound quanta directly, through a technique similar to the photoelectric detection of light. The process is as follows. Cavity *B* of Fig. 8 is irradiated with quanta of microwave radio-frequency energy slightly exceeding the $(-1) \rightarrow (0)$ energy level spacing (solid arrow in the energy level diagram at right of Fig. 8). Under this condition no spin transition occurs. However, when a burst of ultrasonic energy from cavity *A* strikes the spins in cavity *B*, a spin transition, $(-1) \rightarrow (+1)$, will occur if the quantum of sound energy is such as to satisfy the condition

$$h\nu_{rf} + h\nu_{ph} = 2h\nu_o.$$

(Here $h\nu_{rf}$ and $h\nu_{ph}$ are quanta of radio-frequency energy and of ultrasonic energy, respectively.) When this happens, the reflected power appearing at point x decreases, indicating that radio-frequency energy has been absorbed along with sound in the double quantum transition of the spins from (-1) to $(+1)$. Such a transition proceeds regardless of the coherence and geometry of the sound field, provided only that its frequency satisfies the condition expressed in the foregoing equation (*51*).

With most spin systems the probability that such a double-quantum (phonon-photon) transition will occur is quite small, so ultrasonic detection by this means would be insensitive. However, with Fe^{++} and certain other paramagnetic ions the probability is large, because of the strong coupling between spin and sound field. Under these circumstances the detection sensitivity can approach that of ideal piezoelectric detection in quartz. Such a scheme could be particularly useful for detecting quanta and performing spectroscopy at ultrasonic frequencies beyond 10^{11} cycles per second provided appropriate spin energy levels are attainable. Dransfeld has suggested the use of excitons as a possible double-quantum detector of phonons in the thermal spectrum; a secondary peak should occur, displaced from the main exciton peak by an energy corresponding to that of the incident phonon. Undoubtedly other quantum schemes will suggest themselves as research at higher frequencies develops.

Future Research

So far, most of the ultrasonic research at microwave frequencies has been concerned with the development of experimental methods and the extension and refining of earlier results and ideas. In attempting to look ahead it is well to keep in mind two characteristics which distinguish ultrasonic waves from electromagnetic waves. Ultrasonic waves can penetrate relatively thick samples of good electrical conductors, and the selection rules governing various spin, electronic, and vibrational transitions are less restrictive than those governing electromagnetic excitation. Hence, there are more allowed transitions for ultrasonic radia-

tion; this suggests that such radiation can sometimes reveal dynamical processes and states of matter inaccessible to its electromagnetic cousin. These properties will undoubtedly be significant in determining the direction of future work, but only time can fill in the details.

Further exploration within the microwave frequency range now attainable seems applicable to the study of electron-phonon interactions (*52*) in normal metals, superconductors, and semiconductors; elementary excitations in condensed boson and fermion systems (for example, He^4, He^3, and electrons in very pure metals); the dynamics of molecular and ionic impurities in dielectric crystals; and numerous aspects of the liquid state.

At still higher frequencies questions arise concerning (i) the lifetime of thermal phonons in various materials and the relation to thermal conductivity, and (ii) the detailed picture of interatomic forces, particularly in crystals, as revealed by the dispersion of elastic waves of very short wavelength. In the latter connection it would be interesting to see just how well our present notion of simple vibrational normal modes describes the actual vibrational states of crystals, and perhaps even liquids, for frequencies above 10^{12} cycles per second. Although the technique of neutron diffraction has already shed some light on these questions, direct experiments involving elastic wave propagation at thermal frequencies could yield much sharper details.

But all such experiments are going to be difficult and will progress slowly. Ultrasonic radiation is inherently awkward to manage as compared to electromagnetic waves and particle beams: its wavelength and quantum of energy $h\nu$ are small, the attenuation is often large, and good mechanical impedance matching between transducer and sample (particularly if the sample is a liquid) is usually difficult if not impossible in practice (*53*). Nonetheless, some progress in surmounting these experimental problems has been made, and as the motivation for exploring such phenomena develops, suitable means will evolve.

But what of the immediate future? In view of the basic nature of elastic wave propagation, it seems likely that, in the next few years, microwave ultrasonics will be of significance in the study of structural aspects of condensed matter—particularly in the study of structural defects in crystals. In such experiments, elastic waves have an advantage over optical waves in that they can traverse opaque media and are more strongly coupled to the atomic lattice. Even quite mild imperfections of any kind can produce severe scattering of the elastic wave, scattering which is easily detected (*54*). Finally, one might speculate on the possibility of using microwave sound, because of the short wavelength and high frequency, to probe the structure of macromolecules in solution, and the nature of solids under transient, superhigh pressures created by implosion. However, improvement and extension of our present rather cumbersome experimental methods will be needed before we can undertake such investigations.

Summary

It is now possible, by quite straightforward means, to generate and detect elastic waves in solids and, to a limited extent, in liquids, up to frequencies of some 10^{11} cycles per second. Extensions to even thermal frequencies (10^{12} to 10^{13} cycles per second) appear feasible. Such mechanical radiation is highly sensitive to any electronic or structural inhomogeneities, of which there are many, affecting the interatomic forces, attenuation, or local density. In certain cases this sensitivity renders ultrasonic radiation a particularly useful tool for examining various structural properties and dynamic processes in condensed matter. Much wider application of the method seems possible and likely, but awaits further insight and considerable ingenuity on the part of the experimenter.

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56. Support of microwave ultrasonic research in this laboratory by the National Science Foundation and the Office of Naval Research is gratefully acknowledged.

Deuterated Organisms: Cultivation and Uses

Living organisms of unusual isotopic composition can be used for magnetic resonance studies.

Joseph J. Katz and Henry L. Crespi

The element hydrogen occurs in nature as a mixture of nuclei, identical in charge but differing in mass. The predominant light variety of hydrogen, of mass 1, is accompanied by a rare, nonradioactive, heavy isotope of mass 2, which occurs in the proportion of 0.015 parts per 100 parts of ordinary hydrogen. Although, in most cases, the isotopes of an element are very similar in chemical properties, the hydrogen isotopes differ between themselves to an extent that justifies individual names, and the heavy, nonradioactive hydrogen isotope of mass 2 is called deuterium. Hydrogen is present in water and all organic compounds, and is thus an essential component of all living matter. By a "deuterated organism" we mean one in which all the hydrogen present is in the form of the heavy isotope. Not only the cellular water but the cellular components contain deuterium instead of hydrogen. A deuterated organism thus has an unusual relationship to its prototype organism. A deuterated organism is an artifact, for it is to be found nowhere in nature. The hydrogen-containing and the deuterated organisms may differ significantly in morphology, cytochemistry, and biosynthetic capacity, but basically they must be the same organism. By our definition, a deuterated organism is essentially free of ordinary hydrogen, and is able to carry out all metabolic activities essential to life. It is the purpose of this article to describe how deuterated organisms may be grown and how they differ from their prototypes, and to indicate some of the uses to which such organisms (and the compounds that can be derived from them) may be put.

Deuterium was discovered by Urey, Brickwedde, and Murphy (*1*) in 1932. That deuterium would have special significance in biological systems was recognized very shortly after its discovery. The hydrogen isotopes differ more in chemical properties than the isotopes of any other element do (*2*). Consequently, the replacement of hydrogen by deuterium in water and in chemical compounds may result in considerable differences in reaction rate (*3*) and in changes in ionic equilibria (*4*), in water structure (*5*), and in various physical parameters such as vapor pressure (*6*) and infrared spectra (*7*). In more biological systems, substitution of deuterium can affect protein conformation (*8*) and coil-helix transitions (*9*). Some

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