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CURRENT PROBLEMS IN RESEARCH

Acoustic Techniques in Magnetic Resonance

Acoustic coupling to nuclear and electron spins is a measure of relaxation in paramagnetic systems.

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Since its discovery in 1946, the technique of nuclear magnetic resonance (NMR) has become a powerful tool for the study of liquid and solid states. In the case of liquids, high-resolution NMR has developed into an important spectroscopic technique to supplement optical spectroscopy and other analytical chemical techniques (*1*). In the case of solids, it has made fundamental contributions to our understanding of internal interactions among nuclear spins, between nuclear and electron spins, and between spins and thermal motions of the lattice. However, conventional NMR, relying as it does on coupling to the magnetic moments of nuclei by a time-varying radio-frequency magnetic field, cannot be directly applied to certain interesting problems in solid-state phenomena. Let us list the most important of these limitations.

1) Because of limitations of skin depth (a radio-frequency field at 10 Mcy/sec has a depth of penetration of only 0.02 centimeter in copper), conventional NMR cannot be used to investigate metals in bulk or in single crystal form.

2) The study of spin-phonon (*2*) relaxation processes by conventional NMR is complicated by the following factors: (i) there may be several relaxation mechanisms contributing at the same time; (ii) these are often observable only by indirect methods; and (iii) the "direct" spin-phonon interaction is "swamped" by an "indirect" spin-phonon interaction at all but very low temperatures in the liquid helium range.

3) Normally, in NMR, nuclear electric quadrupole interactions can be observed directly only in complex noncubic solids, such as paradichlorobenzene, in which there exists a static quadrupole interaction strong enough to split the high-field NMR line or to be directly observable by the technique of pure nuclear quadrupole spectroscopy. In simple solids, such as sodium chloride, quadrupole effects are observable only indirectly by their effect on the width or shape of the high-field NMR line.

Through acoustic nuclear spin-phonon measurements it is, in theory at least, possible to overcome these three limitations. After a brief introduction to the principles of nuclear magnetic resonance, I will describe the theory and practice of acoustic spin-phonon coupling of both nuclear and electron spins in solids.

That the nuclei of many atoms have magnetic properties has been known for many years. These magnetic properties are associated with the fact that the nucleus as a whole has a spin or angular momentum, I, which makes it act like a small gyroscope. A measure of nuclear magnetism is the magnetic moment μ of a nucleus,

$$\mu = gI \tag{1}$$

where g is the ratio of the magnetic moment to the nuclear spin (*3*). In the presence of an applied magnetic field H_0, the magnetic moment experiences a a torque that tends to align it parallel to the field. As in the case of the gyroscope, the magnetic moment then precesses at an angle θ about the magnetic field as axis (Fig. 1). The angular frequency of precession ω_0, is given by

$$\omega_0 = 2\pi\nu_0 = 2\pi\frac{\mu}{Ih}H_0 \tag{2}$$

where h is Planck's constant.

If a magnetic field H_1, rotating in the same direction as the nuclear precession, is now applied at right angles to H_0 and in the plane of H_0 and μ, the effect will be to tip μ in a direction antiparallel to H_0. This corresponds to an absorption of energy from the source of the perturbing field H_1. Maximum absorption occurs when the rotational frequency of H_1 obeys the resonance condition (Eq. 2). For the I^{127} nucleus ($I = 5/2$, $\mu = 2.79$ nuclear magnetons), the frequency at which resonant absorption occurs in a field of 10,000 gauss (from Eq. 2) is $\nu_0 = 8.52$ megacycles per second.

The presence of Planck's constant in the resonance condition (Eq. 2) is a forcible reminder that systems of nuclear (and electron) spins are quantized. That is, a nucleus with spin I may assume only $2I + 1$ discrete orientations in a magnetic field. These orientations correspond to discrete energy levels characterized by the magnetic quantum number m, the projection of I along the direction of the magnetic field. A pictorial representation of the energy-level scheme for a hydrogen nucleus ($I = 1/2$) is shown in Fig. 2, where n_1, E_1 and n_2, E_2 are, respectively, the number of spins and their magnetic energy in levels 1 and 2. Application of

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a radio-frequency magnetic field (H_1 in Fig. 1) induces transitions between the energy levels. The allowed transitions for a magnetic dipole moment interacting with an external field are those for which m changes by ± 1 ($\Delta m = \pm 1$).

Since the probabilities for transitions between adjacent energy levels are equal for transitions up and down, it might appear at first, that there would be no net absorption of energy (since a "down" transition corresponding to a release of energy from the higher level might be expected to just cancel the absorption of energy in an "up" transition). This would, indeed, be true if the two states were equally densely populated. If, however, an assembly of nuclear moments occupying just two states ($I = 1/2$) is in thermal equilibrium at a temperature T, the lower of the two states will be more densely populated, according to a Boltzmann distribution factor

$$n_2 = n_1 e^{-h\nu/kT} \qquad (3)$$

where k is the Boltzmann constant and $h\nu$ is the energy difference $E_2 - E_1$ between the two levels. The population difference $n_1 - n_2$ is commonly of the order of parts per million. Because of the greater population at the lower energy level, there is a net absorption of energy from the radio-frequency magnetic field. A typical resonance absorption curve is shown in Fig. 2.

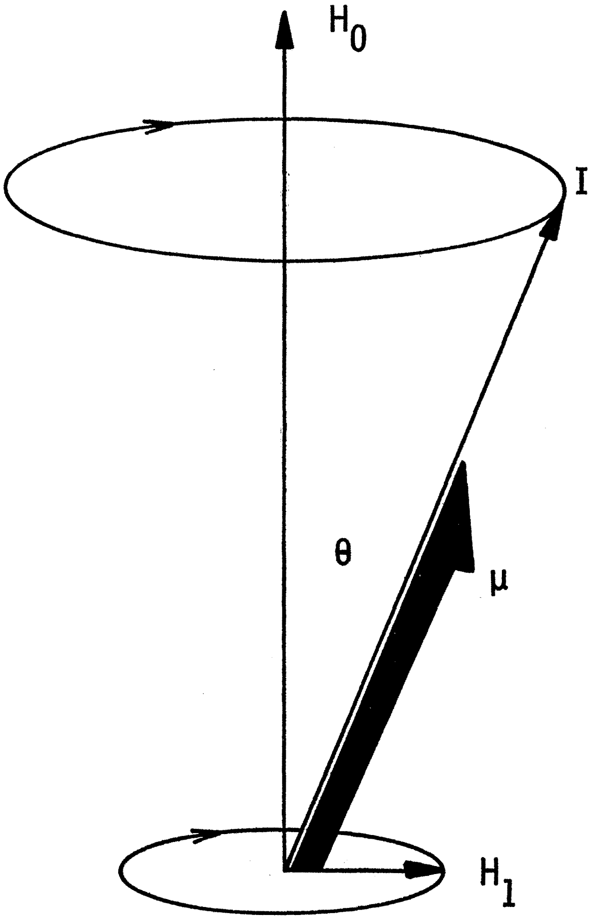
The existence, in the presence of an external magnetic field H_0, of discrete magnetic energy levels and of a distribution of nuclear spin moments among these levels leads to a net macroscopic magnetization in the sample containing these spins. By applying the fundamental Boltzmann law of statistical mechanics, we obtain the expression for the net nuclear magnetization

$$M = \frac{N\mu^2}{3kT}\left(\frac{I+1}{I}\right) H_0 \qquad (4)$$

where N is the total number of spins. It is this net magnetization which is often measured in nuclear magnetic resonance experiments.

An apparatus capable of detecting the nuclear magnetic resonance phenomenon is shown in Fig. 3. The radio-frequency magnetic field is produced by a coil wound round the sample, the whole being located in a uniform magnetic field. The coil forms the inductance of the tuned circuit, which controls the frequency of a marginal radio-frequency oscillator. When the magnetic field is adjusted to resonance (Eq. 2), the additional absorption of energy in the coil results in a decrease in amplitude of oscillation. The amplitude of oscillation is monitored by a sensitive radio-frequency receiver. For display purposes, a set of modulating coils is used to sweep the magnetic field at an audio-frequency rate through the values of field corresponding to resonance. The direct-current magnetic field is swept slowly to display the NMR spectrum on a cathode-ray oscilloscope or on a recording millivoltmeter. More sophisticated instrumentation, incorporating alternating-current synchronous detection techniques, is used in spectrometers designed to detect weak absorption signals.

In the preceding outline of the fundamentals of nuclear magnetic resonance (*4*) there have been several omissions. I would like to rectify only two of these. The first has to do with the fact that nuclei possess not only magnetic moments (due essentially to moving charges in the nucleus) but also electrical moments. The lowest nonvanishing electrical moment is the electric quadrupole moment, which is a measure of departure from spherical symmetry of the charge distribution in the nucleus. Only nuclei with spin $I > 1/2$ have nonvanishing electric quadrupole moments. The



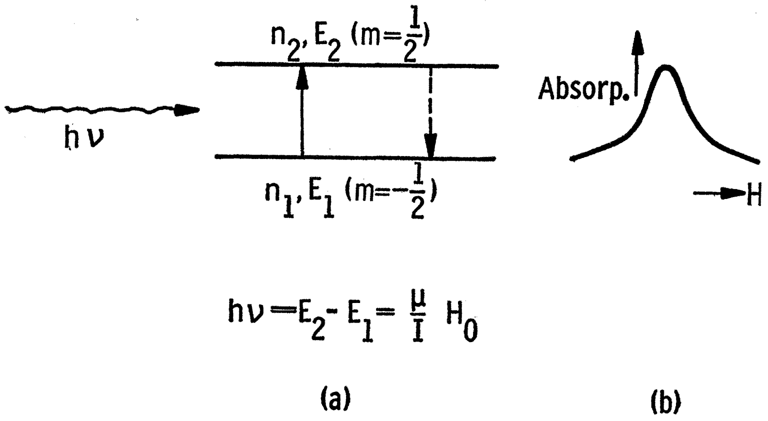


Fig. 1 (left). Gyroscopic precession of a nuclear magnetic moment μ about the axis of an externally applied magnetic field H_0. I is the nuclear spin. A rotating magnetic field H_1 tends to increase the angle θ between the magnetic-moment vector and the field axis.

Fig. 2 (above). *a*, Energy levels for a nucleus with spin $I = 1/2$—for example, hydrogen. *E*, *n*, and *m* represent the energy level, population, and magnetic quantum number, respectively. Transitions between levels are induced by radio-frequency energy $h\nu$. *b*, A typical nuclear-magnetic-resonance absorption line. The intensity of absorption is plotted as a function of direct-current magnetic field H (at constant frequency).

nuclear electric quadrupole moment, *Q*, interacts with electric field gradients (inhomogeneous electric fields) which exist at the nucleus as a result of neighboring electrical charges, such as those of electrons external to but associated with the nucleus. In the common case of axial electric field gradients, this electric-quadrupole-interaction energy may be denoted by the scalar quantity e^2qQ, where $q(=\partial E/\partial z)$ is the field gradient along the axis of symmetry and e is the charge of the electron.

The electric quadrupole interaction is of importance for several reasons. It is often responsible for the frequency widths of NMR lines, thus determining the ease or difficulty with which such lines are detected. It may result, in the case of quadrupolar nuclei occupying noncubic sites in a molecule or crystal lattice, in the splitting of the NMR line. One can, indeed, observe transitions among energy states which are characteristic of the internal quadrupole interaction alone. The resonance line obtained is then called a pure nuclear quadrupole resonance absorption line (*4*). Furthermore, the electric quadrupole interaction can give valuable information on the nature of chemical bonding in molecules and crystals. It can be shown from the detailed expression for e^2qQ that spherically symmetric distributions of charge do not contribute. Since inner electron shells are, to a first approximation at least, spherically symmetric, the magnitude of e^2qQ is determined primarily by the valence electrons. The valence electrons are, of course, those electrons primarily responsible for the bonding characteristics of an ion in a molecule or crystal. Most important of all, perhaps, is the fact that the internal quadrupole interaction is in many nonconducting crystals the most effective contact between the nucleus and the lattice.

The second omission is the concept of spin-lattice relaxation, the mechanism by which nuclear spins do, in fact, couple energy to the thermal motions of the crystal lattice. The discussion of this concept, basic to the technique of acoustic coupling to nuclear spins, deserves a section to itself.

Spin-Lattice Relaxation

The process of magnetic resonance absorption described above is predicated on the availability of an excess of nuclear spins in a lower energy state over nuclear spins in a higher energy state. The effect of the externally applied radio-frequency magnetic field is to "pump up" spins from a lower to a higher energy level. Were there no counterbalancing process, this would result in an equalization of the populations of the levels. The counterbalancing process is provided by the interaction between spins and "lattice." By *lattice* is meant the material in which the nuclear spins are embedded.

In a crystal the nuclei are at fixed lattice sites; their movement arises from the lattice vibrations (phonons) characteristic of the temperature of the crystal. This thermal lattice motion acts to

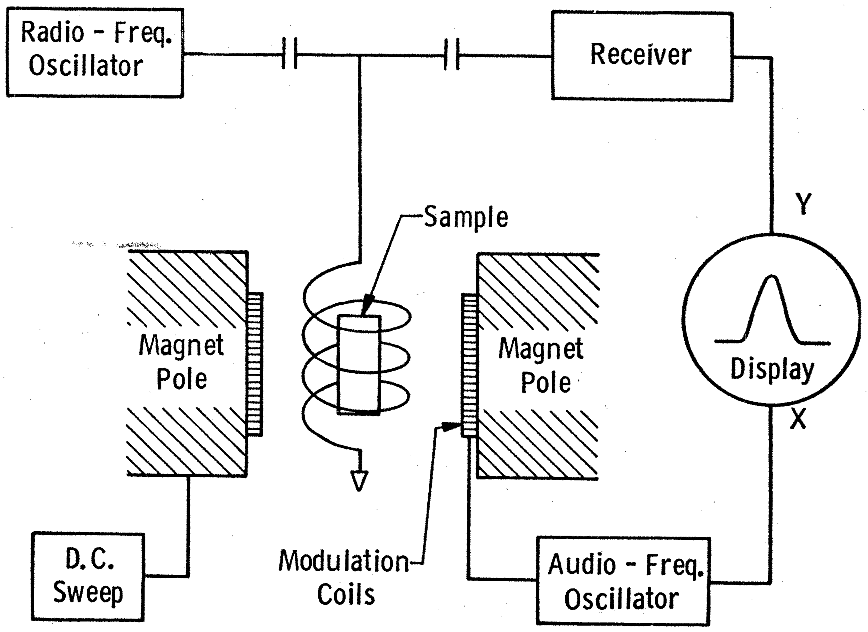


Fig. 3. Schematic diagram of the NMR spectrometer. The radio-frequency magnetic field is produced by a coil which forms part of the tank circuit of a marginal oscillator. The coil and specimen are placed between the magnet poles. Absorption of radio-frequency energy by spins results in a decrease in the amplitude of oscillation across the coil, which is monitored by a sensitive receiver. The resonance line may be displayed on an oscilloscope or recorder (not shown).

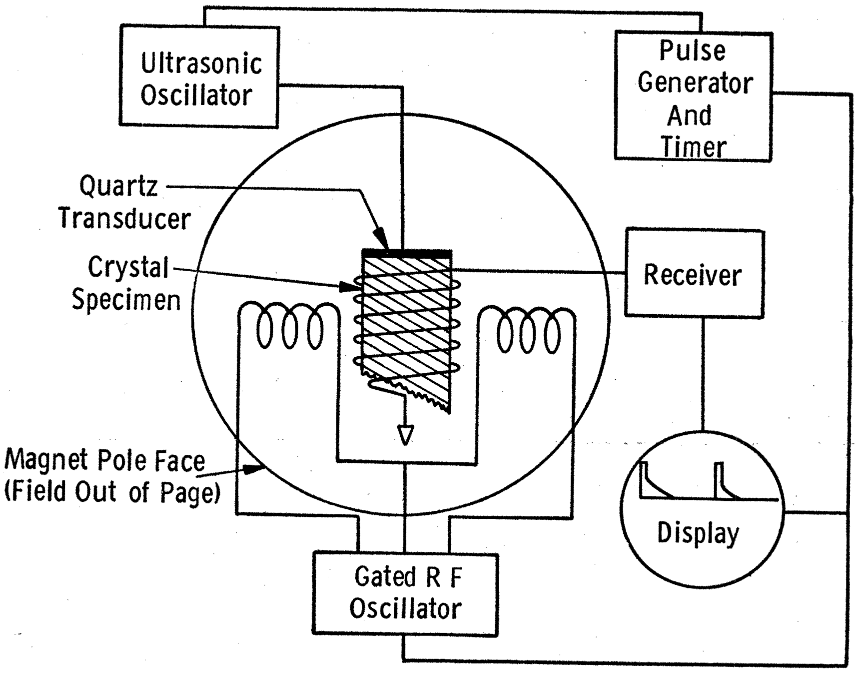


Fig. 4. Schematic diagram of an NMR pulse spectrometer for observing acoustic saturation effects. Acoustic energy is introduced by means of a quartz piezoelectric crystal bonded to the sodium chloride specimen. The effect on the pulse NMR display is observed on the oscilloscope.

keep the distribution of the nuclei among the states of different energy at its equilibrium value. The characteristic time required for a spin system to attain an equilibrium distribution after disturbance of this distribution is called T_1, the spin-lattice relaxation time. If the contact between the spin system and the lattice is small (that is, if T_1 is long), the excited spins cannot give up their extra energy rapidly enough, the net absorption decreases, and we say that "saturation" results.

For the lattice vibrations to be able to couple energy to and from the nuclear spin system, an interaction between the two systems must be provided. Nature provides this in the form of internal nuclear magnetic or electric interactions whose strength is modulated by the effect of the lattice vibrations. Thus, in many dielectric crystals, such as the alkali halides (with nuclei of spin greater than ½), it is the internal electric quadrupole interactions which provide the necessary interaction. The elastic vibrations of the lattice periodically modify the electric field gradient at the nucleus so as to transfer energy to or from the nuclear spin system.

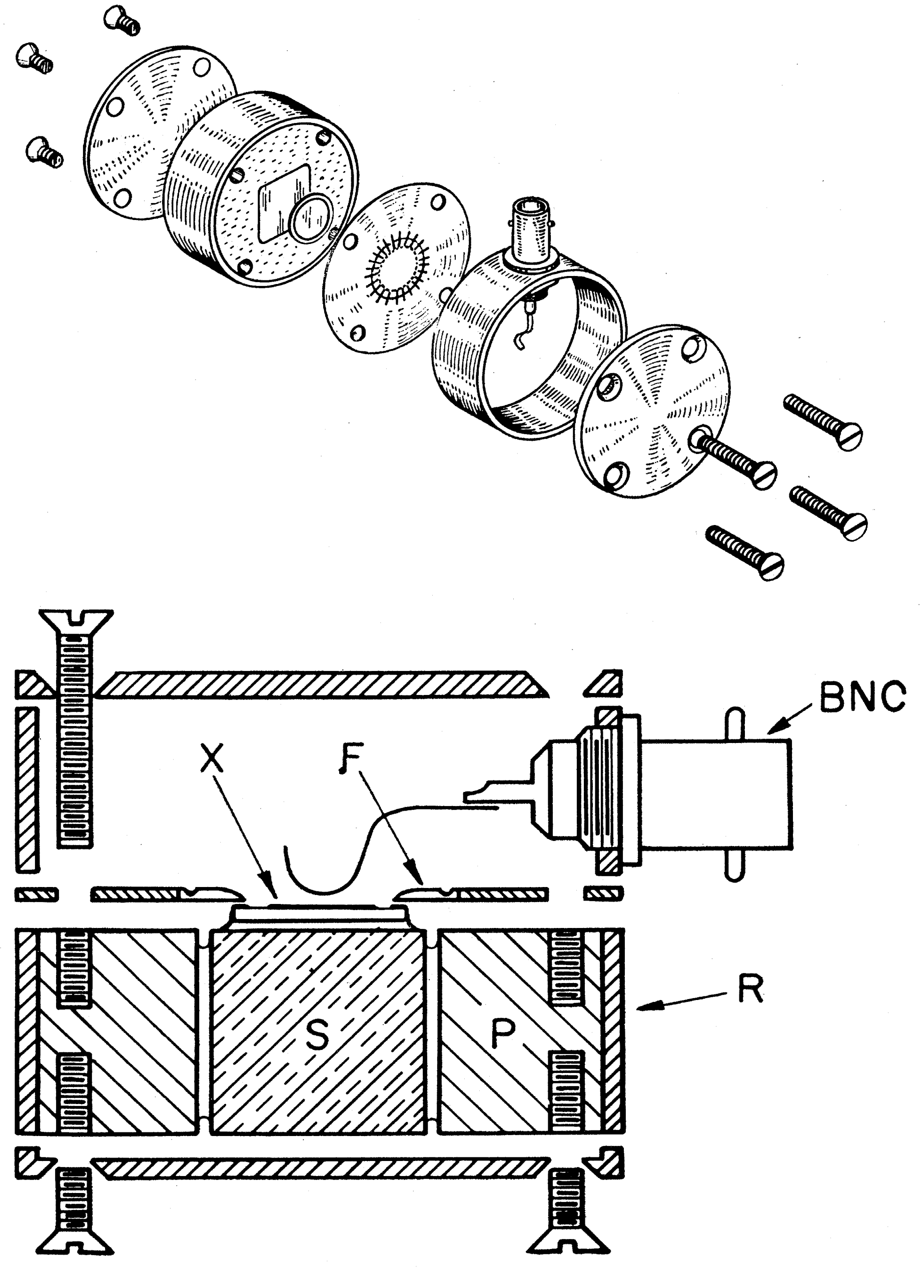


Fig. 5. Ultrasonic probe used in direct acoustic technique. (Top) Assembly. (Bottom) Cross section: *S*, specimen whose end faces have been optically polished; *X*, piezoelectric quartz transducer bonded to specimen; *F*, spring washer to make ground contact to transducer; *P*, plastic holder; *R*, aluminum can for purposes of radio-frequency radiation shielding; *BNC*, radio-frequency connector for cable to matching network and marginal oscillator.

Whatever internal field is being modulated, the energy exchange between lattice and spin system occurs primarily through two mechanisms. In the first, a lattice vibration of energy equal to the energy of excitation $E = h\nu_0$ (or $2h\nu_0$) of the nuclear magnet may be emitted or absorbed, depending upon whether a nuclear spin is excited or de-excited in the process. This "direct" spin-lattice interaction is effective in the relaxation process only at very low temperatures. At higher temperatures, the "indirect" spin-lattice mechanism predominates. This is a scattering process in which one lattice vibration is absorbed and a second lattice vibration is emitted during the interaction with the nuclear spin, the difference in energy of the two lattice vibrations being equal to the nuclear spin energy $h\nu_0$ (or $2h\nu_0$). This is the more probable relaxation process since it involves all the lattice vibrations characteristric of the lattice at a given temperature, while the direct process involves only "resonant phonons"—that is, lattice vibrations whose frequency equals the resonant absorption frequency of the nuclear spins.

The existence of the direct spin-lattice interaction led Kastler, in France (*5*), and later Al'tshuler, in the U.S.S.R. (*6*), to predict that the inverse process—the absorption by the nuclear spin system of energy from an externally generated acoustic wave—should be observable. They reasoned that the acoustic waves, like resonant lattice vibrations, should periodically modulate an internal interaction, such as the quadrupolar interaction, thus exchanging energy with the nuclear spin system. Since very intense acoustic waves at radio frequencies could be introduced into the sample, the intensity of the acoustic coupling could be made quite strong even at elevated temperatures at which the direct resonant spin-lattice interaction was negligible. This "internal resonance" due to phonon-spin coupling could be observed in two ways, they said. The most direct method would be observation of resonant absorption of energy from the source of the acoustic phonons. A less direct method would be observation of the effect of the acoustic phonons on a nuclear magnetic resonance line. In the latter case, a saturation (decrease in intensity) of the NMR line would occur because the available excess spins in the lower energy level would be decreased by the combined action of radio-frequency and strong acoustic excitation.

Acoustic Saturation

The first experiments to demonstrate acoustic coupling to nuclear spins were performed by Proctor and his collaborators in 1955 at the University of Washington (*7*). These experiments were of the saturation type described—that is, the type in which the acoustic coupling was observed by its effect on a conventional nuclear magnetic resonance absorption line. The effect of the acoustic waves was determined by monitoring the magnetization of the nuclear spin system by means of a pulse technique. In this pulse technique a short pulse of radio-frequency magnetic field H_1, at the resonant frequency, is applied to a coil surrounding the specimen. Application of this pulse results in a transient radio-frequency pulse from the spin system which is proportional in magnitude to the nuclear magnetization of the system just before the pulse was applied. The nuclear magnetization is, as explained earlier, a function of the populations of the various energy states. The alteration of these populations by the acoustic phonons results in a decrease in nuclear magnetization and therefore a decrease in the height of the transient pulse.

The arrangement of an experiment on sodium chloride (*8*) by the pulse saturation technique is shown schematically in Fig. 4. A pulse generator-timer, radio-frequency oscillator, and receiver and display unit (oscilloscope) comprise a conventional pulsed nuclear magnetic resonance spectrometer. The separate transmitter and receiver coils surrounding the specimen are mutually perpendicular. The novel feature in the experiment was the application of ultrasonic energy. This was accomplished by exciting an *x*-cut (longitudinal mode) quartz piezoelectric transducer, bonded to one end of the sample, by means of a radio-frequency power oscillator. The ultrasonic frequency was adjusted to equal twice the resonant frequency (about 10 Mcy/sec) in order to minimize the possibility of spurious excitation by the radio-frequency field driving the transducer. An attempt was made, by making all surfaces but the top surface of the specimen irregular, to scatter the ultrasonic waves into an isotropic distribution, and thus to produce a uniform acoustic energy density.

The effect of the ultrasonic waves on the nuclear magnetization was measured by inserting a long (8-second) ultrasonic pulse between two of the short radio-frequency pulses which sampled the nuclear magnetization, as already described above. The pulse heights were observed to be a function of the amplitude and frequency of the radio-frequency field driving the quartz transducer. From these data one could determine the frequency width of the acoustic absorption, and also the strength of the coupling ("transition probability") of the ultrasound to the nuclear-spin system.

A quantitative interpretation of the acoustic saturation data requires a knowledge of the amplitude, wavelength, and polarization of the ultrasonic vibrations. In the experiment with sodium chloride an attempt was made to estimate the amplitude of vibration from the acoustic power transmitted to the sample and from the decay time of the ultrasonic excitation (phonon relaxation time). The latter quantity, in particular, was not well known for the particular specimen under investigation. The resultant uncertainty in the derived value for amplitude of acoustic vibration is perhaps the greatest drawback to the technique described.

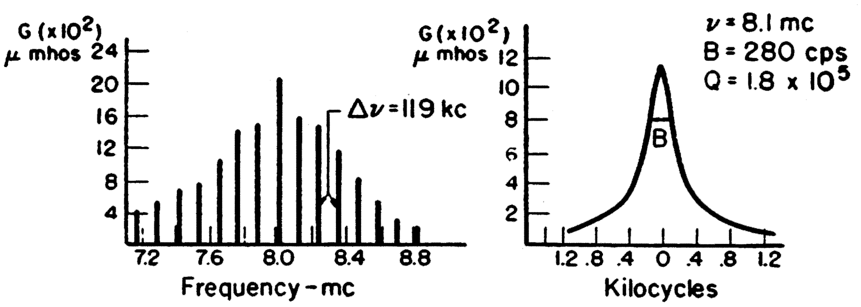


Fig. 6. Example of a sharp line frequency spectrum typical of composite acoustic resonator. *G* (equivalent electrical conductance of resonator) is a measure of energy input to the specimen. At right, one of the mechanical resonance lines in detail.

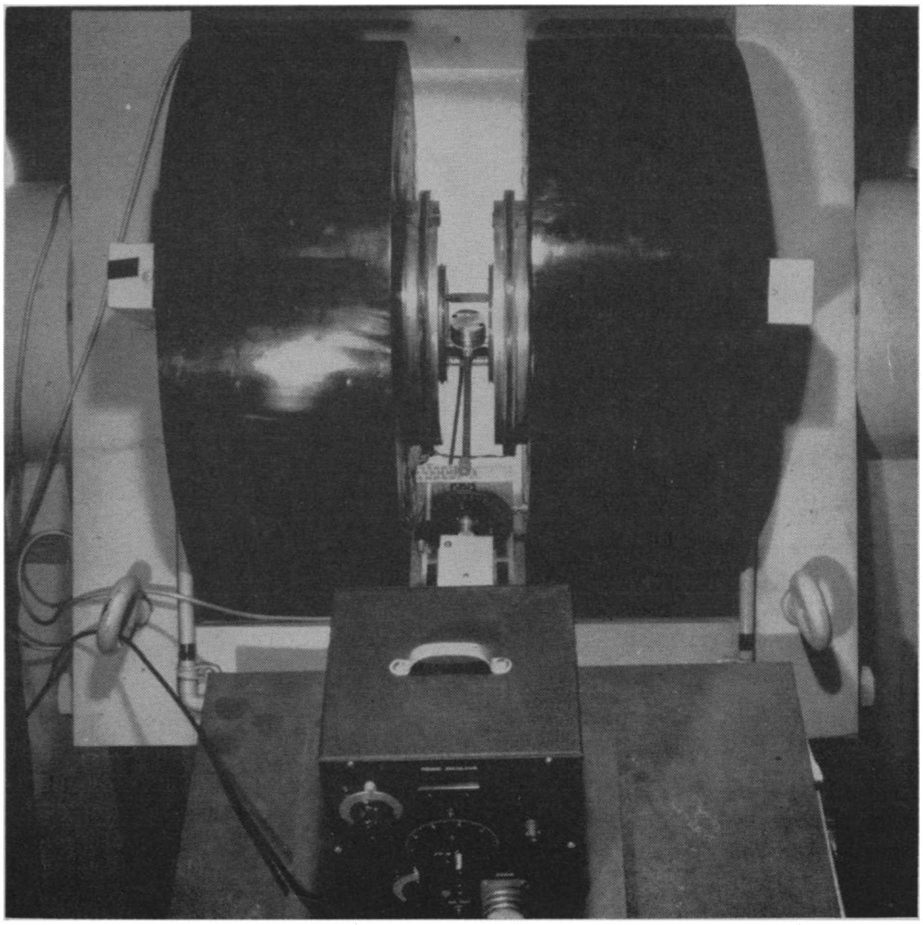


Fig. 7. Magnet, modulating coils, and essential components of the acoustic spin-phonon spectrometer: acoustic probe containing specimen, orienting drum, matching network, and marginal oscillator.

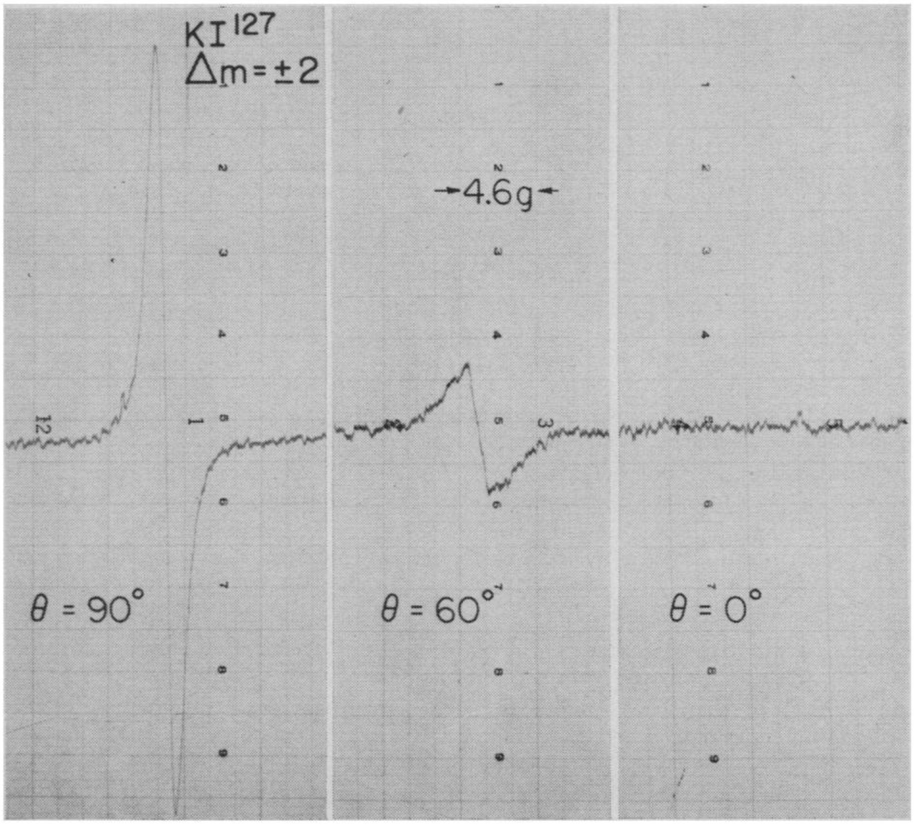


Fig. 8. Recorder traces of acoustic spin-phonon absorption lines of I^{127} in potassium iodide. The traces are first derivatives of the actual absorption lines. Θ, Angle between the acoustic strain axis and the direction of the external field. The strong dependence of line intensity on Θ has been explained (*11*) as due to the angular dependence of the quadrupolar transition probability and to the preferential distribution of static strains along certain crystallographic directions.

To circumvent the latter difficulty, alternative techniques have been used. One is to select a specimen, such as sodium iodide, in which acoustic coupling to both sets of nuclear spins, Na^{23} and I^{127}, can be measured (*9*). The results can then be expressed in terms of the ratio of strengths of acoustic coupling. This ratio, although not as informative as a knowledge of the absolute values of the spin-phonon coupling constants, can be used to obtain information on the relative chemical bonding of the Na^+ and I^- ions in the sodium iodide crystal.

A second technique, used by Taylor and Bloembergen (*10*) to study ultrasonic saturation of Na^{23} and Cl^{35} spins in sodium chloride, is to monitor the acoustic-energy density by the variation in capacitance of a capacitor whose electrodes are the end face of the specimen and a fixed, charged reference plate. The average displacement of the free end face of the specimen was measured by the change in total capacitance. Calibration of the capacitance was difficult, however, and uncertain to within a factor of 2 or so. In this experiment a continuous-wave technique was used. A spectrometer of marginal oscillator type was used to monitor the NMR absorption line with and without the application of ultrasonic energy (again at twice the resonant frequency) to the specimen. A comparison of line intensities in the two cases enabled one to estimate the strength of acoustic coupling to the spin system. A similar technique has been used recently by Silver to study I^{127} nuclear spins in potassium iodide (*11*). He has, in addition, detected changes in the nuclear magnetization by an ultrasonic amplitude-modulation technique.

Direct Acoustic Excitation of Nuclear Spins

In all the experiments described in the previous section, the interaction of ultrasound with nuclear spins was observed indirectly by its effect on a conventional NMR line. Conventional NMR, let me say again, couples to the spins through the interaction of a radio-frequency magnetic field and the magnetic moment associated with the nuclear spin. An NMR absorption is evidenced as an absorption of energy from the source of the radio-frequency magnetic field. An exact analogy in the ultransonic case is the case in which *only* ultrasonic energy is used to couple to the nuclear spins, this coupling being observed as an absorption of energy from the source of ultrasound. We dispense with the radio-frequency coil shown in Figs. 3 and 4 and call this technique "direct acoustic excitation of nuclear spins."

The question posed for the experimenter seeking to detect this direct acoustic coupling is, How is one to measure the very small change in acoustic power due to resonant absorption by the nuclear-spin systems? Conventional ultrasonic pulse-echo techniques (*12*) are capable of detecting changes in acoustic attenuation in solids of about 1 part in 10^{-3}. This is sufficient sensitivity for measuring background attenuation in many solids; the attenuation coefficient, in good acoustic materials, is of the order of 10^{-2} per centimeter. The background attenuation is a function of type of material, state of strain, imperfections, and so on. The attenuation coefficient due to nuclear-spin–phonon coupling, however, was expected to be of the order of 10^{-7} to 10^{-8} per centimeter. Obviously, something better than the conventional techniques had to be used.

The solution arrived at (*13*) was to combine a continuous-wave ultrasonic composite-resonator technique with nuclear magnetic resonance techniques. The composite resonator, shown in Fig. 5, consists of the sample, which has been ground and polished to have optically flat and parallel end faces, and a quartz piezoelectric transducer bonded to one face of the sample. The frequency response of this ultrasonic composite resonator consists of a sharp line spectrum, such as that shown in Fig. 6. The spectrum is characteristic of a resonant standing wave pattern, individual lines corresponding to mechanical resonances of the sample (that is, a resonant response occurs when the frequency is such that the length of the composite resonator is equal to an integral number of half wavelengths of sound). For a crystal having low acoustic attenuation (such as an alkali halide), each mechanical resonance line will have a high Q, where Q (the "quality factor") is a measure of the sharpness of the resonance line.

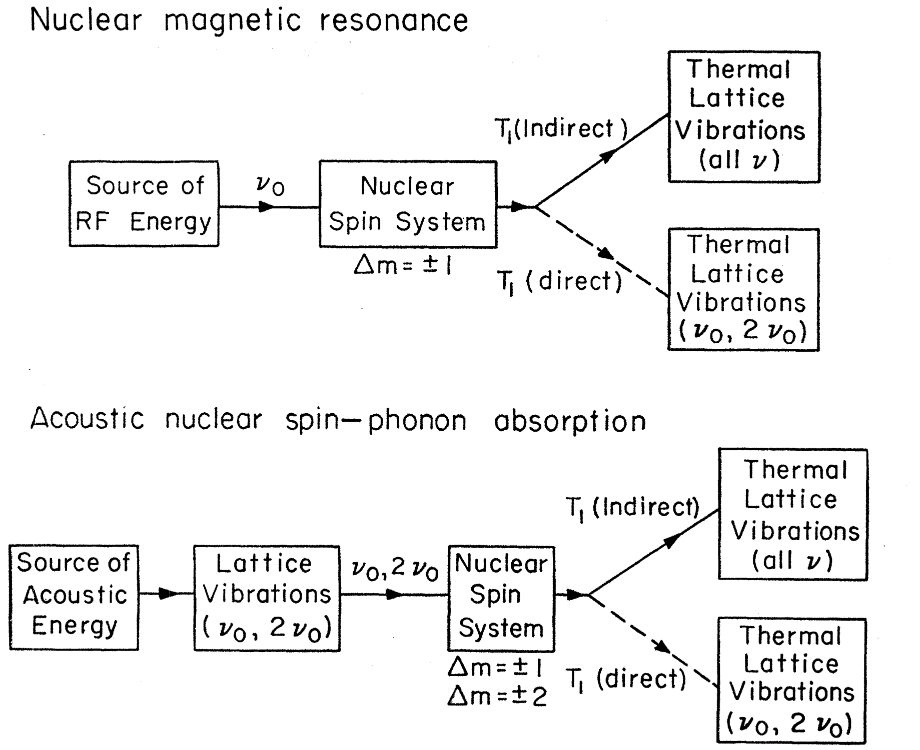


Fig. 9. A comparison of conventional NMR and acoustic excitation of nuclear spins. The mechanisms of excitation differ markedly; the relaxation processes, however, are the same, except possibly at very low temperatures.

The composite resonator is coupled to a marginal oscillator, such as that used in conventional NMR spectrometers, by means of a special radio-frequency transformer and matching network. When the oscillator is adjusted to a frequency corresponding to a mechanical resonant line of high Q, it will "lock in" to this frequency and be effectively converted into a crystal-controlled oscillator. The amplitude of radio-frequency across the tank circuit of the oscillator can be made responsive to losses in the acoustic probe. Thus, if an additional small attenuation in the sample occurs, it will be detected as a decrease in oscillation level. This additional attenuation occurs when the magnetic field is adjusted to a value corresponding to a nuclear-spin resonance. An overall view of acoustic probe, matching network, oscillator, and magnet is given in Fig. 7.

A difficulty inherent in the acoustic saturation technique—that of determining the acoustic energy density in the specimen—is overcome by the direct excitation technique. If we call α_n the coefficient of acoustic attenuation due to the nuclear-spin system, then the power-absorption coefficient is given by

$$2\alpha_n = P_n/P_0 \qquad (5)$$

where P_n is the power per unit volume absorbed by the nuclei and P_0 is the power per unit area in the acoustic wave. The power density in the acoustic wave is given by

$$P_0 = \rho(v^3\delta^2)/2 \qquad (6)$$

Here ρ is the density of the material, v is the velocity of the acoustic wave, and δ is the peak value of the time-varying strain caused by the sound wave. In the materials thus far investigated, the power absorbed by the nuclei depends essentially on the square of an internal interaction, such as the electric quadrupole interaction, which itself is proportional to the strain δ. This follows from the fact that it is the time-dependent part of the internal interaction which is responsible for the acoustic spin-phonon coupling, and the effectiveness of this time-dependent interaction is proportional to the strain caused by the acoustic wave. With $P_n \propto \delta^2$, from Eqs. 5 and 6, we see that α_n will be independent of δ.

The remaining acoustic parameters which enter into the expression α_n, such as sound velocity, background attenuation, effective cross-sectional area of the acoustic beam, and the equivalent electrical resistance of the acoustic probe, are obtained by means of standard ultrasonic continuous-wave (*14*) and pulse-echo (*12*) techniques. From a knowledge of these parameters and of the electrical characteristics of the matching circuit, the radio-frequency output of the marginal oscillator, at a particular temperature and frequency, can be calibrated in terms of α_n. From the behavior of α_n as a function of magnetic field, temperature, acoustic power input, and orientation of the specimen in the magnetic field, one can obtain information concerning the nature and strength of internal interactions involving nuclear spins.

Since the mechanism of coupling to the nuclear spins by direct ultrasonic excitation differs so markedly from the radio-frequency magnetic field coupling of the conventional nuclear magnetic resonance technique, it is not surprising that the resulting spectra also differ greatly. The quantum-mechanical selection rules, determining among which energy levels spin transitions may be induced, differ for the two cases. The transition probabilities, which determine the intensities of the allowed resonance lines, differ as well. As a result of these fundamental differences, the resonance line width, shapes of lines, and dependence of line intensity on angle Θ between magnetic field axis and crystal axis will also differ markedly. These differences have been verified for the cases of two classes of crystals: alkali halides [such as potassium iodide (*15*)] and group III–V semiconductor crystals [such as indium antimonide (*16*)]. Typical spectra observed as a function of Θ are shown in Fig. 8. Because an alternating-current magnetic field modulation, phase-sensitive detection technique is used, the recorded lines are first derivatives of the actual absorption line.

Finally, in this brief summary of the direct acoustic excitation technique, it should be remembered that, except possibly at very low temperatures, the relaxation mechanisms in the cases of conventional nuclear magnetic resonance and acoustic spin-phonon coupling should be the same. This is indicated in Fig. 9, in which the differences in coupling mechanisms are also illustrated. As was explained briefly in the section on spin-lattice relaxation, the excited spin system may relax by an "indirect" process involving the entire spectrum of nonresonant phonons, or by a "direct" process involving only resonant (ν_0 and $2\nu_0$) phonons. Since the latter process is effective only at very low temperatures, in the liquid helium range, it is indicated by a dashed line in Fig. 9.

Results and Discussion

How well have acoustic-magnetic-resonance techniques been applied to the solutions of the problems cited at the beginning of this article? In the application to bulk conductors, acoustic nuclear spin-phonon coupling has not yet been observed in metals, although there are several obvious candidates among metal single crystals currently available. Although measurements have not yet been made on metals, they have been made on single crystals of semiconductors such as InSb (*16*). In the latter case, the skin-depth limitation has been overcome by the use of acoustic instead of radio-frequency energy; moreover, from a comparison of the relative line intensities of the antimony isotopes Sb^{121} and Sb^{123} (*17*), certain interesting conclusions can be drawn. From a comparison of the nuclear properties of the antimony isotopes, we obtain the inequalities

$$\frac{\mu_{Sb}{}^{121}}{\mu_{Sb}{}^{123}} > 1$$
$$\frac{Q_{Sb}{}^{121}}{Q_{Sb}{}^{123}} < 1 \qquad (7)$$

As observed by the conventional NMR technique, the Sb^{121} line is more intense than the Sb^{123} line; the latter, being wider, is difficult to observe at any but low temperatures. The width of the line is primarily due to static quadrupolar broadening as a result of electric field gradients located about lattice imperfections. As observed by direct acoustic coupling, the Sb^{123} line is more intense than the Sb^{121} line, and both are easily observable at room temperature in a large single crystal of InSb. This is direct proof that the acoustic coupling is by way of a quadrupolar interaction (rather than, say, a magnetic dipole-dipole interaction). We can also conclude that the relaxation mechanism (the reverse of our acoustic spin-phonon mechanism) also proceeds by way of the quadrupolar interaction, and that Sb^{123} will have a shorter T_1 (a higher relaxation rate) than Sb^{121}. The latter conclusion has indeed been verified for antimony isotopes in AlSb (*18*).

Table 1. Percentage covalent bonding $z\lambda$ of I^{127} ions in the alkali iodides from dynamic quadrupole couplings and from chemical shifts.

	R_o (A)	e^2q_1Q (Mcy/sec)	γ_1	$z\lambda$(%) from e^2q_1Q	σ (10^{-4})	$z\lambda$(%) from σ
LiI	3.00				3.3	11.2
NaI	3.23	660	69	8.5	1.2	4.0
KI	3.52	300	38	3.5	1.0	3.3
RbI	3.66	615	80	7.0	1.7	5.5
CsI	3.95	1600	200	16.5	5.0	16.5

Nuclei in conductors come to thermal equilibrium with the lattice primarily through the mediation of the conduction electrons—via nuclear-electron hyperfine coupling. In dielectric materials containing sufficient numbers of paramagnetic impurities, which are much more highly coupled to the lattice than are the nuclei, the nuclei again will relax, primarily through these impurities. In dielectrics sufficiently free of paramagnetic impurities, however, nuclear spin-lattice relaxation occurs through either of the two internal interactions which are modulated by lattice vibrations: magnetic dipole-dipole interaction and nuclear electric quadrupole interaction. The latter mechanism predominates for all nuclei which have sizable quadrupole moments. For nuclei with spin equal to ½ (that is, with spherically symmetric nuclear charge distribution and hence no quadrupole moment), the magnetic dipole-dipole relaxation mechanism prevails by default. I have shown above that in the case of antimony in indium antimonide the relaxation is quadrupolar in nature. The distinction between the two types of relaxation can be made more general by investigating the dependence of the direct acoustic absorption on the angle Θ between the strain axis due to the acoustic wave and the axis of the external magnetic field. This has been done for the nuclei Br^{79}, Br^{81}, I^{127}, In^{115}, Sb^{121}, and Sb^{123} in the alkali bromides and iodides, and in InSb. In all instances the direct acoustic coupling, and therefore the spin-lattice relaxation mechanism, is quadrupolar in nature.

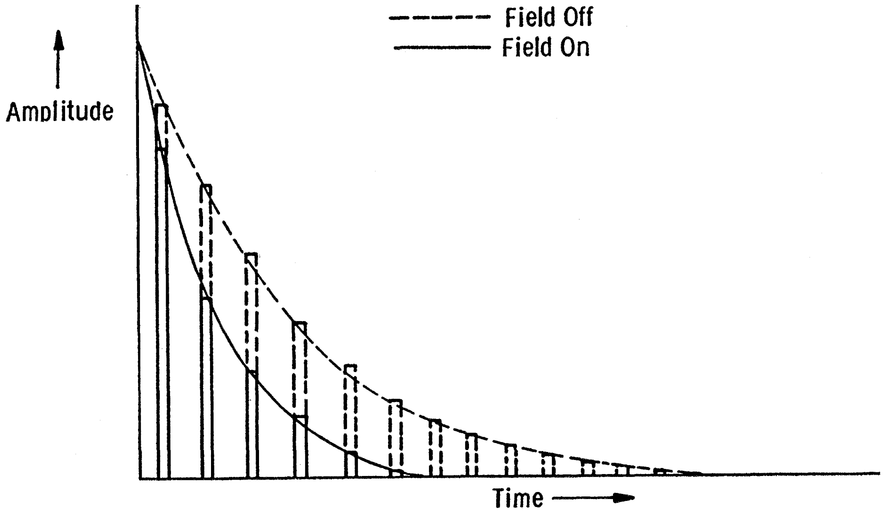


Fig. 10. Pulse-echo technique of observing electron spin-phonon coupling at hypersonic (microwave) frequencies. When the resonant magnetic field is applied, the acoustic attenuation in the specimen increases because of the excitation of electron spins.

Abragam and Proctor (*19*) used the ultrasonic saturation technique on a crystal of sodium chloride in a study of the role of spin-spin interactions in establishing and maintaining a Boltzmann distribution among the populations of the spin system. In particular, they were able, by raising the intensity of the acoustic input power, to make the net magnetization resulting from the Na^{23} spins disappear completely.

The principal results to date of the acoustic spin-phonon experiments have been the quantitative measurement of the magnitude of the dynamic nuclear quadrupole interaction, eq_1Q. The evaluation of eq_0Q, where q_0 is the static electric field gradient, depends essentially on the electron charge density in the crystal. The evaluation of eq_1Q, where q_1 is the first derivative with respect to strain of the electric field gradient, involves the dependence of the electron density distribution upon the lattice deformation. In the cubic alkali halide crystals q_0 is zero, and q_1 is the field-gradient term entering into the expression for the acoustic spin-phonon interaction. Regardless of whether q_0 or q_1 is involved, however, the same model must be invoked to explain the magnitude of the quadrupolar interaction.

Various models have been proposed to explain the quadrupolar interactions observed in ionic crystals. The first and simplest is the point-charge model, which assumes that the electric field gradient at a nuclear position is caused by point charges at the positions of the neighboring ions. The magnitude of these charges is taken as γ times an ionic charge, where γ is an open parameter. The dynamic quadrupole interaction e^2q_1Q is then due to the displacement of these charges by the time-varying distortion of the crystal. The observed values of γ for heavy halide nuclei such as bromine and iodine are considerably larger than unity (see Table 1). This means that the internal electric-field gradients are too large to be accounted for solely by the charges on the neighbor ions and must therefore be due to electronic charges in the ion itself. Since the closed-shell configuration of the free ion is spherically symmetric (and therefore cannot contribute to q_1) the quadrupolar interaction must be due to a deformation of the ion—that is, to a departure from a closed-shell configuration. The dynamic quadrupole interaction e^2q_1Q may be ascribed to the change in the ion deformation when the crystal is strained.

Quantitative agreement between values of γ predicted theoretically (*20*) and values obtained experimentally is not good. We are forced to conclude, in fact, that explanations of the quadrupolar results based on a purely ionic model of the crystal are not adequate. An explanation based on covalent effects has been presented by Yosida and Moriya (*21*). In their theory the deformation of the electron cloud of the ion (I^- in our case) is assumed to be representable as the excitation of an electron in an outer *p* orbital to a higher state. The electric field gradient at the halide nucleus is then primarily due to the hole left in the *p* orbital. The amount of admixture of the excited state, λ, is left as an open parameter to be determined by comparison with experimental data. The dynamic quadrupole coupling e^2q_1Q is then due to the variation of λ with internuclear spacing. Menes and Bolef (*15*) give a more detailed discussion of the experimental application of this theory.

According to Yosida and Moriya, the chemical shift in NMR also depends on λ and may be used to determine it. The chemical shift (*1*) is the fractional change in the local magnetic field at the nuclear position, due to the second-order paramagnetism of the surrounding electrons; the latter depends, in turn, upon the distortion of the ion charge distribution. The observed chemical shift can thus be used to estimate this distortion, or (in terms of our covalent model) the amount of excited state admixture λ. Since the chemical shift is easily measured and is known for the alkali iodides (*15*, *22*), it provides a good independent measure of the λ obtained from the dynamic quadrupole coupling data. A comparison is made in Table 1, in which the results on the alkali iodides are summarized. Column 1 gives the undistorted lattice internuclear separations R_0 in angstroms; column 2, the experimentally determined values of e^2q_1Q; column 3, the values of the so-called shielding factor γ_1, based on the ionic model; column 4, the degree of covalency ($\equiv z\lambda$, where z is the number of nearest neighbors to the halide ion); column 5, experimentally determined values of the chemical shift σ; and column 6, the degree of covalency as determined from the chemical shift. A comparison of $z\lambda$ from columns 4 and 6 indicates that the quadrupole coupling and the chemical shift of the iodine nucleus in alkali iodide crystals can indeed be explained on the basis of an admixture of excited states to the ionic configuration.

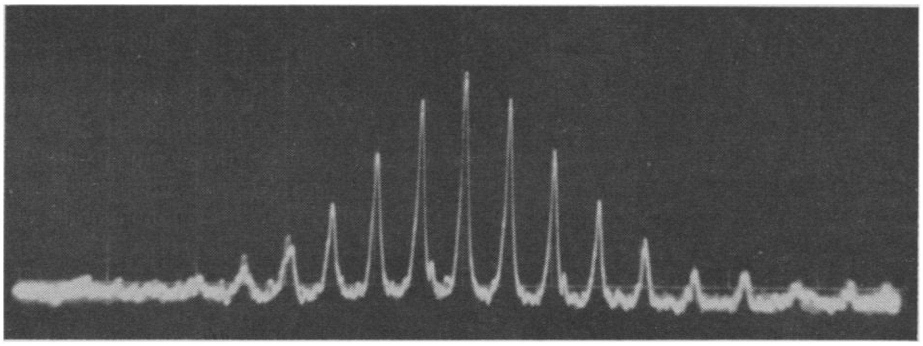


Fig. 11. Continuous-wave mechanical resonance spectrum of ruby at 440 megacycles and 4°K, obtained with overtone quartz piezoelectric transducers. The *Q* of the lines is of the order of 5000 at low temperatures.

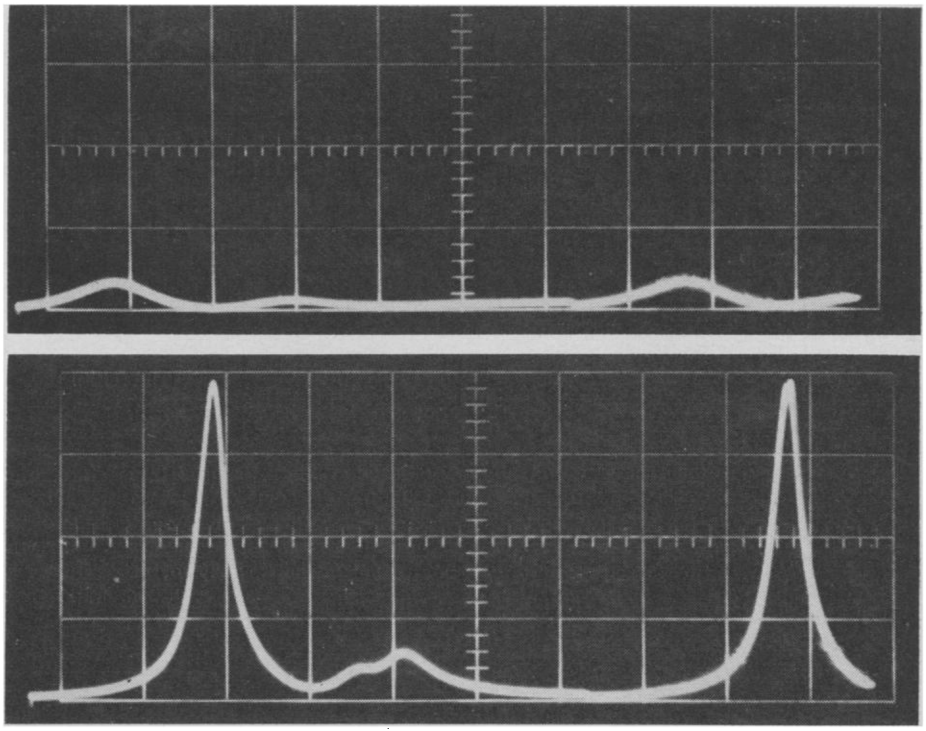


Fig. 12. Electron-spin phonon coupling of Fe^{2+} ions in magnesium oxide at 200 megacycles and 4°K. (Bottom) Field off; (top) field on at 200 gauss. This intense spin-phonon absorption occurs in concentrations of the order of 100 parts of Fe^{2+} per million in magnesium oxide and has a line width of several thousand gauss at low temperatures.

Acoustic Coupling to Electron Spins

We have thus far restricted our discussion of acoustic techniques in magnetic resonance to nuclei. Electrons, however, also have magnetic properties which are important to an understanding of solid-state phenomena. Since acoustic electron spin-phonon coupling has been observed mostly for paramagnetic ions, we will restrict our discussion to the electrons associated with these ions.

Electron paramagnetic resonance is analogous to NMR in the sense that it involves transitions among a given set of energy levels, due to the coupling between the electronic magnetic moment and an alternating radio-frequency magnetic field. As in the case of NMR, the energy level separations are a function of magnetic field. For a free electron, indeed, a resonance condition identical to Eq. 2 can be written if we substitute the electron spin (S = ½) for I and the electron magnetic moment μ_e for μ_n. Since μ_e is greater than μ_n by about three orders of magnitude, the resonant frequencies involved fall in the ultrahigh-frequency or microwave regions for available laboratory magnetic fields.

For all but the very special case of the free electron, however, the problem is much more complicated. It is complicated by the fact that the electron spins associated with paramagnetic ions are subject not only to an external magnetic field but also to crystalline electric field effects through coupling of the spin and orbital angular moments. The combination of these interactions leads in general to complicated energy-level configurations. The relaxation effects are also complex, depending not only upon the electronic ground state of the ion but also on the proximity of excited electronic states.

The two mechanisms responsible for coupling nuclear spins to the thermal lattice vibrations, however, apply also to the coupling of electron spins to the lattice. In general, the direct spin-lattice relaxation mechanism (involving thermal phonons at the resonance frequency ν_0, or at $2\nu_0$) predominates in the liquid-helium temperature range. At higher temperatures the indirect spin-lattice relaxation mechanism dominates. At 4°K, the spin-lattice relaxation time varies from a fraction of a second (for example, for Cr^{3+}) to microseconds (for example, for Fe^{2+}).

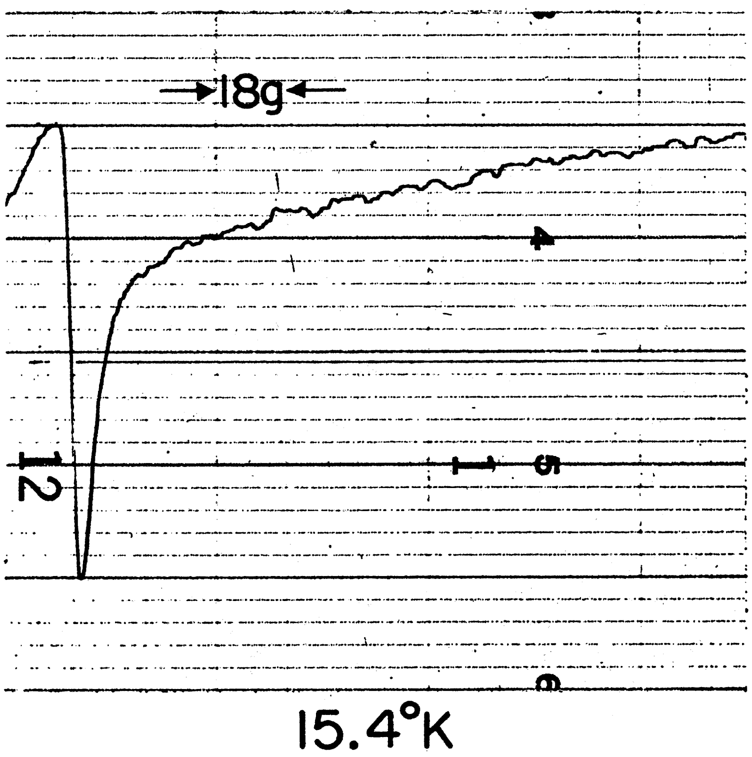
As for the case of phonon coupling to nuclear spins, Kastler and Al'tshuler also pointed out the importance of direct phonon coupling to electron spins. In particular, one might hope through measurement of spin-phonon coupling coefficients to increase our rather meager understanding of the detailed interactions responsible for electron spin relaxation to the lattice temperature. It can be shown, in fact, that there is a simple relationship between α_D, the direct acoustic absorption coefficient, and T_{1D}, the direct spin-lattice relaxation time (*23*):

$$\frac{1}{T_{1D}} = \alpha_D \frac{{}^{4}\pi}{h^2} \frac{(kT)^2}{nv^2} \Delta\nu \qquad (8)$$

where n is the density of paramagnetic ions, v is the velocity of sound, and $\Delta\nu$ is the half-width of the spin-phonon resonance line.

The first experiments demonstrating acoustic coupling to electron spins were, as in the nuclear case, of the saturation type, in which the effect of the introduction of externally generated acoustic waves was monitored by the decrease in intensity of a conventional electron paramagnetic resonance line (*24*). This technique has produced valuable data (*25*) for such details as the angular variation of the spin-phonon transition probability, but it does not readily produce a quantitative measure of the spin-phonon coupling constant.

Two techniques have been used to achieve observation of direct acoustic coupling to electron spin paramagnetic ions. The first, a pulse-echo technique, is intimately connected with a striking advance made in recent years in the generation and propagation of acoustic waves at very high frequencies. Baranskii (*26*) in the U.S.S.R. and Bömmel



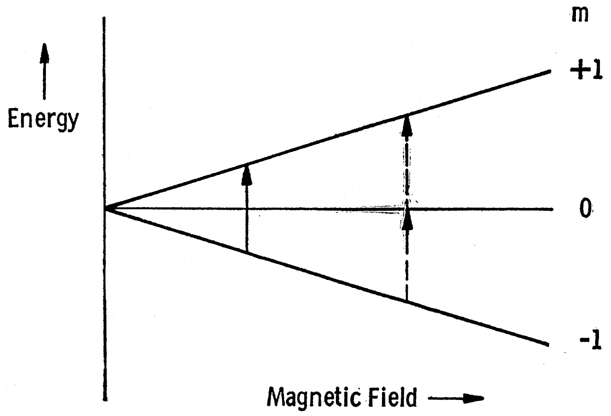


Fig. 13 (left). Narrow spin-phonon absorption line observed in magnesium oxide containing Fe^{2+} ions in concentrations of about 20 parts per million. These data were recorded at 200 megacycles and 16°K for longitudinal waves propagated along a cube axis, and represent $\Delta m = \pm 2$ transitions between the $m = -1$ and the $m = +1$ energy levels of Fe^{2+} in magnesium oxide.

Fig. 14 (above). Magnetic energy levels of Fe^{2+} ions in cubic magnesium oxide. The levels are denoted by the magnetic quantum number m.

and Dransfeld (*27*) in the United States showed that acoustic waves at microwave frequencies could be produced in a rod of single crystal quartz placed in a microwave cavity so that an end surface was exposed to an intense microwave electric field in the cavity. Bömmel and Dransfeld pointed out that the free surface of the piezoelectric quartz crystal in the microwave electric field can be regarded as a transducer of high-frequency acoustic ("hypersonic") waves, while the remainder of the rod acts only as a transmission medium. At the other end of the rod, also located in a cavity, the acoustic energy is reconverted into electromagnetic energy.

Because of the very strong coupling to the lattice of the electron spins, it becomes feasible at microwave frequencies to observe direct spin-phonon coupling by straightforward pulse-echo techniques. This was done by Tucker (*25*) at 9100 megacycles per second for $\Delta m = \pm 1$ transition of Cr^{3+} ions in single crystals of Al_2O_3 (ruby). A diagrammatic sketch of the observed effect is given in Fig. 10. When the magnetic field was adjusted to a value corresponding to the appropriate resonance condition, an increase in attenuation was observed, as indicated by the solid curve. The measured attenuation at 1.5°K of longitudinal mode waves propagated along the c axis of the crystal was 4×10^{-2} per centimeter.

The second technique (*28*) is an extension to higher frequencies of the continuous-wave resonance technique described earlier. An acoustic transmission probe, similar to that shown in Fig. 5 but having transducers on both polished ends of the specimen, is used. A frequency-swept ultrahigh-frequency signal generator is used to drive the transmitting transducer at a harmonic of its fundamental frequency. A pattern such as that shown in Fig. 11 for ruby (Al_2O_3 doped with Cr_2O_3) at 440 megacycles per second is obtained. The Q, or sharpness of the mechanical resonance lines, thus displayed is a measure of the background attenuation typical of the crystal being investigated.

If the resonant absorption due to the interaction of high-frequency phonons and electron spins is intense, one may see the change that occurs in the pattern of Fig. 11 when a magnetic field is applied. This is shown in Fig. 12 for Fe^{2+} ions (concentration, approximately 100 parts per million) in single crystals of magnesium oxide. This extremely large absorption has not yet been explained. If, as is more than likely to be the case, the acoustic coupling to electron spins is small at these frequencies, one must resort to a much more sensitive continuous-wave spectrometer. This spectrometer is the acoustic analog of a conventional electron paramagnetic resonance transmission spectrometer. In the latter, the resonant change in Q of a microwave cavity in which the paramagnetic specimen is placed is recorded as a function of magnetic field. In the acoustic counterpart the built-in mechanical resonance acts as a "cavity" —that is, one adjusts the continuous-wave oscillator (no longer frequency-swept) to the frequency of one of the mechanical resonance peaks. This corresponds to a condition of maximum sensitivity to changes in absorption. A sensitive, low-noise receiver is then used to detect small changes in Q due to spin-phonon coupling as the magnetic field is varied through the range corresponding to resonance.

An example of an electron spin-phonon resonance absorption line of Fe^{2+} in magnesium oxide obtained by this continuous-wave technique is shown in Fig. 13. As in Fig. 8, the recorded lines, because of the magnetic-field-modulation technique used, are first derivatives of the actual absorption lines. The measurements were made with 40-Mcy/sec quartz transducers driven at their 5th harmonic. The resonance display is due to $\Delta m = \pm 2$ transitions, normally forbidden in electron paramagnetic resonance, between the $m = +1$ and the $m = -1$ energy levels of the Fe^{2+} ion. The energy-level scheme for this ion, shown in Fig. 14, is particularly simple when the ion is in a cubic environment, as it is in magnesium oxide. The measured acoustic coupling coefficient at 200 megacycles and at a temperature of 4°K was $\alpha_D \cong 10^{-7}$ per centimeter.

Conclusions

In conclusion, I believe it fair to say that the marriage of ultrasonics and magnetic resonance holds promise of being a productive one. In the application of these disciplines to nuclear spins, little more has been done than to demonstrate the acoustic techniques and to apply them to a particular problem of quadrupolar coupling in the heavy alkali halides. Particularly promising is the extension of acoustic NMR techniques to bulk metals, to ferromagnetic crystals, and to the study of spin-lattice relaxation as a function of temperature. In the technique of phonon coupling to electron spins in paramagnetic materials, also, the reports to date have all been of a preliminary nature. Used in combination with the powerful new hypersonic technique of generating microwave acoustic waves, electron spin-phonon interaction measurements may help to resolve some of the present confusion regarding the mechanisms of spin-lattice relaxation in paramagnetic solids (*29*).

References and Notes

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2. The word *phonon* is used to designate a quantized elastic wave or lattice vibration of the crystal; the quantum of energy, as in the case of the photon (quantum of electromagnetic energy) is equal to $h\nu$, where h is Planck's constant and ν is the frequency.
3. In Eq. 1, I is in units of $h/2\pi$ (where h is Planck's constant) and μ is in units of nuclear magnetrons, $eh/4\pi Mc$, where e is the electronic charge, M is the rest mass of the proton, and c is the velocity of light.
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29. I thank J. de Klerk and D. W. Feldman for reading the manuscript. Much of the work reported in this article was done in collaboration with M. Menes.