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Electric field effects in RUS measurements

Timothy W. Darling [a,*], Bradley Allured [a], James A. Tencate [b], Michael A. Carpenter [c]

[a] University of Nevada, Reno, NV 89557, USA
[b] Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[c] Cambridge University, Cambridge, England, UK

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ABSTRACT

Much of the power of the Resonant Ultrasound Spectroscopy (RUS) technique is the ability to make mechanical resonance measurements while the environment of the sample is changed. Temperature and magnetic field are important examples. Due to the common use of piezoelectric transducers near the sample, applied electric fields introduce complications, but many materials have technologically interesting responses to applied static and RF electric fields. Non-contact optical, buffered, or shielded transducers permit the application of charge and externally applied electric fields while making RUS measurements. For conducting samples, in vacuum, charging produces a small negative pressure in the volume of the material – a state rarely explored. At very high charges we influence the electron density near the surface so the propagation of surface waves and their resonances may give us a handle on the relationship of electron density to bond strength and elasticity. Our preliminary results indicate a charge sign dependent effect, but we are studying a number of possible other effects induced by charging. In dielectric materials, external electric fields influence the strain response, particularly in ferroelectrics. Experiments to study this connection at phase transformations are planned. The fact that many geological samples contain single crystal quartz suggests a possible use of the piezoelectric response to drive vibrations using applied RF fields. In polycrystals, averaging of strains in randomly oriented crystals implies using the "statistical residual" strain as the drive. The ability to excite vibrations in quartzite polycrystals and arenites is explored. We present results of experimental and theoretical approaches to electric field effects using RUS methods.

1. Introduction: elasticity and RUS

At a microscopic level the elasticity of a material is the inclination of a material to return to a minimum energy configuration through the directed forces of the bonds of each atom to its surrounding neighbors. The change in energy, ΔU, due to a deforming influence can be described by an expansion in the size of the deformation strains e_{ij} around a local equilibrium (stress free internal state) [1]

$$\Delta U = \frac{1}{2} c_{ijkl} e_{ij} e_{kl} + \frac{1}{6} c_{ijklmn} e_{ij} e_{kl} e_{mn} + \ldots \quad (1)$$

where the c_{ijkl} constants form the elastic modulus tensor which represent the sum of the effects of the local elastic restoring forces and conform to the overall symmetry of the system. The c_{ijklmn} are the third order elastic constants resulting from the third strain derivative of the energy (1), and can be also written as the strain derivatives of the second order elastic constants, c_{ijkl}. The restoring force implied in (1) can be written in a linearized form as Hooke's law with stress tensor τ_{ij},

$$\tau_{ij} = c'_{ijkl} e_{kl} \quad (2)$$

where for small strains around the same local equilibrium as (1) $c'_{ijkl} = c_{ijkl}$, but the primed values may be different if a new local equilibrium with a different value of strain is chosen (say by changing the temperature) with the new value determined by the strain and the third order elastic constants.

Resonant Ultrasound Spectroscopy [2] uses the fact that the resonance frequencies of an homogeneous object are determined by the geometry, density, and the restoring forces implied by (1) of the object. Since geometry and density can be accurately measured independently the resulting small strain elastic vibrations can be well described by the wave equation solution using the tensor linear elastic constants. Measurements of the resonance frequencies made under varying conditions can be compared to approximate solutions to arrive at the most consistent values of c_{ijkl} [3].

Fig. 1 shows the principle of a RUS measurement in block diagram form. A sinewave oscillator provides a drive signal for an

* Corresponding author. Tel.: +1 775 784 1685.
E-mail address: darling@unr.edu (T.W. Darling).

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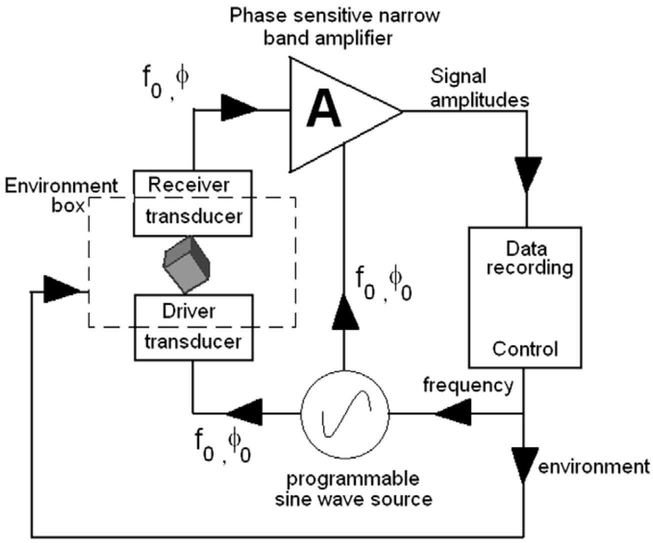

Fig. 1. RUS block diagram. The frequency is stepped in small increments over the desired range. The measurement duration at each step reflects the time to reach a stable amplitude, $\sim Q/f$ and averaging to reduce random noise. Frequency sweeps are made at each value of the environment variable, temperature or magnetic field, for example.

electromechanical transducer and a reference for the detector. A narrow bandwidth homodyne receiver detects the signal due to the resulting amplitude of vibration of a sample at the frequency it is being driven. The maxima in this amplitude at resonance frequencies of the sample produce the spectrum that is used in RUS analysis [4]. This is a linear detection scheme, although simple modifications enable detection of higher harmonics generated through nonlinear processes. The drive and detection process can be done through a variety of means. In the original configuration, piezoelectric transducers made light point-contacts with the corners of a well characterized rectangular parallelepiped (RP) [2,3,5]. The compliance of the small cross section corner contacts decouples the sample sufficiently for free boundary conditions to apply. The transducers themselves are often macroscopically compliant [6] to account for large size/shape changes which can occur at phase changes in a sample. Due to the weak coupling, RUS relies on resonant amplification of the drive vibration to make a detectable signal for the receiver transducer [2,5]. Samples with low "Q" (high dissipation) often make poor RUS samples. The weak sample coupling means we can apply environment "forces" such as temperature change and magnetic field without concern for generation of differential strain at the mounting, from, for instance, differential thermal expansion. The modes of vibration (which are the lowest frequency phonons) become mixed by the boundaries so the actual vibration shapes are complex and usually mixtures of transverse (shear) and longitudinal or bulk waves. The lowest frequency modes are dominated however by the lowest elastic constants, normally shear modes, which can create difficulty in collecting sufficient information on compressional modes.

In general the power of this technique lies in both its frequency resolution and the ability to produce both qualitative and quantitative information on the changes in the local equilibrium state as the sample environment is changed. Qualitative information is usually directly measured from the behavior of the measured frequencies, while quantitative elastic constants are derived from a fitting procedure based on an approximation for the forward problem of determining frequencies from known elastic constants and sample parameters of a freely vibrating body [3]. Changes in both the strain and the restoring forces influence the elastic constants so that both first order and continuous phase transition will be apparent as either a discontinuity or a break in slope of the behavior of the frequencies or the elastic constants.

2. Electric field effects and RUS

There is a great deal of interest in the coupling between electric fields and the elastic state of many materials because the internal charge distribution depends on the electric field and is directly connected to the structure and properties of the materials. The microscopic level properties of materials are fundamentally determined by the extremely strong electromagnetic fields ($E \sim 10^{10}$ Vm^{-1}!) near atomic nuclei and the quantum statistics of the electrons, so the action of external electric fields on materials is of fundamental interest in the way it polarizes (deforms) bound charge configurations and moves the "free" charges in metallic conduction bands.

The strains appearing from the application of an electric field can also be expanded in the applied field [7].

$$e_{ij} = d_{ijk}E_k + \gamma_{ijkl}E_kE_l + \cdots \tag{3}$$

where the d_{ijk} are piezoelectric constants which are nonzero for materials of appropriate symmetry and produce a linearly dependent strain with E, and the gammas are electrostrictive constants which are nonzero for most materials but the quadratic dependence on E means that the effect is sign independent and usually smaller than any piezoelectric effects. In metallic conductors the major influence is flow of charge j according to Ohm's law, where σ_{ij} is the conductivity tensor

$$j_i = \sigma_{ij}E_j \tag{4}$$

This description (3) is incomplete for many actual experimental arrangements. Where fields are applied through charged surfaces attached to the materials, a direct Coulomb force between charges will produce additional strain in materials [8,9]. There are also many nonlinear effects which must be dealt with, for instance the many linear "constant" tensors appearing in the equations below (adapted from [7]) may themselves depend on one or more the of the

$$\begin{aligned}
\Delta S &= \left(\frac{C}{T}\right)\Delta T + p_iE_i + q_iH_i + \alpha'_{ij}\sigma_{ij}\\
D_i &= p'_i\Delta T + \varepsilon_{ij}E_i + \lambda_{ij}H_j + d_{ijk}\sigma_{jk}\\
B_i &= q'_i\Delta T + \lambda'_{ij}E_j + \mu_{ij}H_j + Q_{ijk}\sigma_{jk}\\
e_{ij} &= \alpha_{ij}\Delta T + d'_{ijk}E_k + Q'_{ijk}H_k + s_{ijkl}\sigma_{kl}
\end{aligned}$$

applied fields (ΔT, E, H, σ_{ij}) or responses (ΔS, D, B, e_{ij}). Experiments must constrain the effects of temperature changes, magnetic fields and external stresses [7] to reveal the influence of the electric field on the microscopic properties of materials. A small but curious electronic effect is the inertia of conduction electrons, which produces small currents in longitudinally accelerating metals and small voltages in standing wave systems [10].

3. RUS measurements and applications

External electric fields are not commonly applied in RUS experiments largely due to sample orientation issues and unwanted coupling to piezo transducers. Electroelastic coupling effects are commonly measured using pulse-echo techniques where orientation is controllable, but none of the experimental challenges for RUS are insurmountable. These challenges include; producing a uniform field over the size of the sample and orienting it with respect to the symmetry of the sample, producing a sufficiently high field, shielding transducers from spurious pickup, making the effects of conducting contacts negligible in current

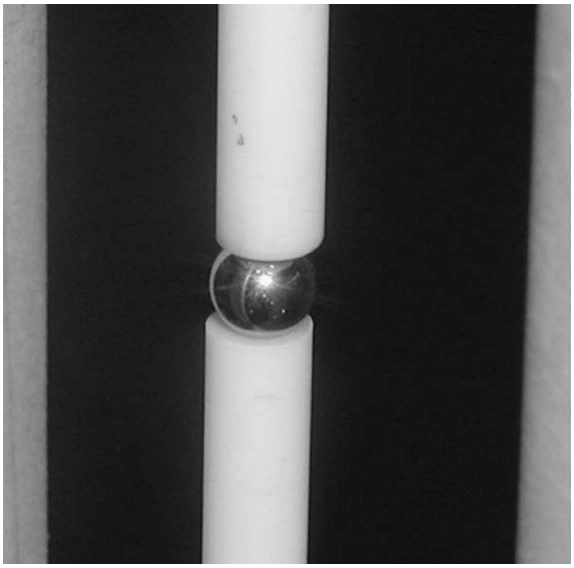

Fig. 2. We are using alumina buffer rods to transport the acoustic signal to transducers that are safely distanced from the high voltage.

flow experiments. RUS analysis of piezoelectric sample resonances must be done with a modified elastic model which distinguishes the piezoelectric effects from the purely elastic ones [11–13]. In a metallic conductor the application of an electric field E causes currents to flow according to Ohm's law. If there is a source of charge and a circuit, the metal will support a steady current and remain locally neutral. The influences of Ohmic heating, strain due to magnetic self-compression, and electromigration of defects all influence the elasticity. In those conductors with a charge density wave (CDW), there is often an additional contribution to the elasticity when the electric field exceeds a threshold value and the CDW becomes "unpinned" and slides through the lattice [14]. Measuring these effects implies contacts for current to flow through the sample, which in general is not useful for RUS, but if we are not seeking the actual values of the elastic constants and are interested in the qualitative behavior of resonances, then lightweight contacts can be tolerated. Many studies of CDW behavior are made with a "diving board" vibration mode and a lightweight contact at the antinode. Clearly with single mode systems one can also locate a nodal position to attach contacts with minimal influence on the sample. This is much more difficult with 3-D samples. If a metal sphere of radius R is statically charged by a current connection or by addition of a beam of charged particles to a voltage V, the sample will experience an expanding pressure ΔP given by,

$$\Delta P = V^2\varepsilon_0/2R \tag{5}$$

This is an extensional strain due to the repulsion of like charges at the surface [8], which is an odd situation (in vacuum, a "negative" pressure) and we expect that bulk resonance frequencies will decrease. For a voltage of 10 kV, the pressure is only about 10 Pa, even with large third order elastic constants this is a very small effect. With excellent temperature control and a synchronous excitation–detection experiment it could well be detectable in a RUS measurement. If the charge is sufficiently high and the condition of internal neutrality demands that the excess (or deficit) charge be at the surface, then the electron density in some depth from the surface and thus the metallic bonding will be altered, which has a direct influence on local elasticity.

We are using a buffer rod [5] approach, Fig. 2, to measure a high grade ball bearing at voltages up to 40 kV. An issue we have to compensate for is the electron field emission at high negative charge and field ion emission at high positive charge. Electron field emission from sharp points on the surfaces of the charging line to the ball is apparent in the HV current draw at about −2 kV. We have found the particles in a cured silver paint are particularly effective at emitting electrons.

Resonances involving high frequency Rayleigh waves [15] should be able to discern the surface strain states, which are likely to be different for electron excess and deficit. The bulk modes respond to a volume strain which is the same for both charge states so these should change frequency in the same sense, independent of the sign of the charge. Modes which are predominantly surface displacing – high frequency spheroidal to Rayleigh wave modes – might change asymmetrically.

Our preliminary result, Fig. 3, on a 6.3 mm diameter solid steel sphere shows a nearly 300 Hz increase in a 2.6 MHz spheroidal

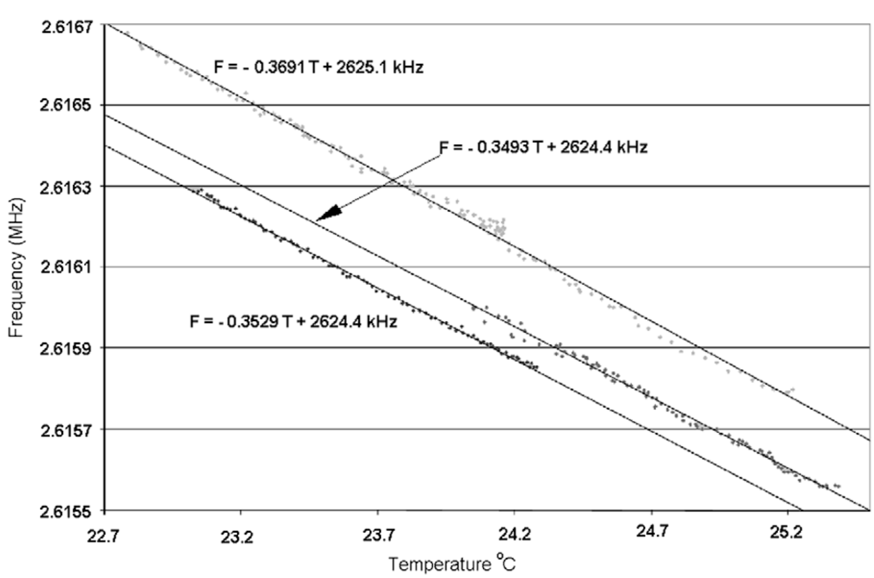

Fig. 3. Frequency changes, in air, for a 2.6 MHz spheroidal mode on a charged ball bearing, as a function of temperature. Upper line: −10 kV; middle: 0 V; lower line: +10 kV. Full scale: y-axis, 1.2 kHz; x-axis, 3.0 °C.

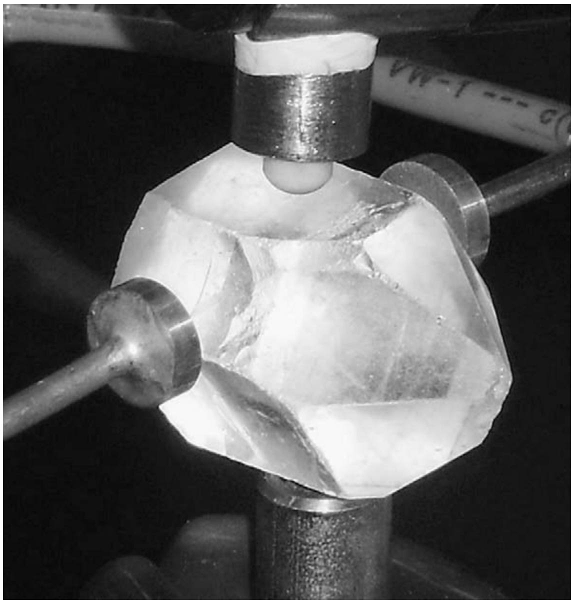

Fig. 4. A quartz crystal driven in a non-contacting mode by the electric field between two plates.

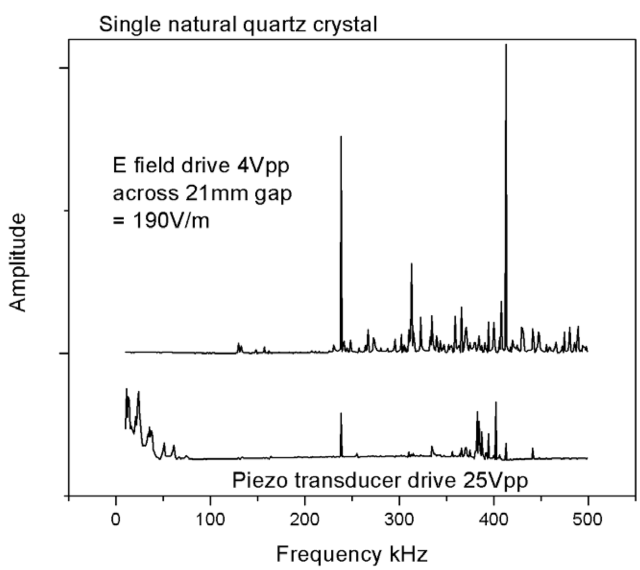

Fig. 5. Resonances of a natural quartz crystal. The external electric-field drive produces a cleaner spectrum than a point contact drive.

mode. The negative linear dependence of the frequency on temperature is as expected [16] and provides confirmation that the mode identity does not change. Application of −10 kV raises the resonance frequency by about 200 Hz and +10 kV decreases it by about 100 Hz. The temperature dependence of the mode does not change. The total frequency change for 20 kV is about 25% of the change produced by a 3 °C temperature change. We are currently involved in preparing RUS measurements on charged spheres in high vacuum (10^{-7} Torr) and at higher frequencies (up to 8 MHz) to examine these effects free from the issue of atmospheric contaminants and with Rayleigh waves of smaller penetration depth. This experiment could link an acoustic measurement to the electron density and bonding at the surfaces of metals when we have eliminated possible surface chemistry effects.

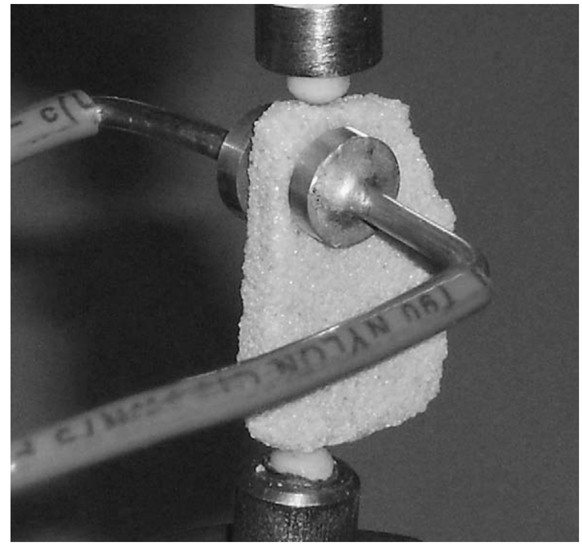

Fig. 6. Driving vibrations in sandstone through the internal strains generated by a high electric field.

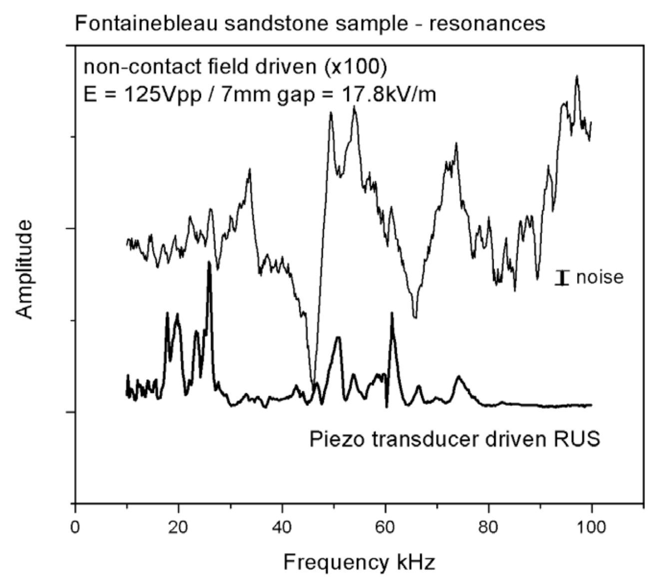

Fig. 7. Although at much smaller amplitude, the piezoelectric generated strains drive resonances in sandstone. If the driving field is not applied across the sample there is no signal and the noise level is as indicated.

4. Driving RUS experiments

When samples can be driven directly through the piezoelectric or electrostrictive effects there is some advantage for the distribution of modes apparent in RUS experiments. The quartz crystal in Fig. 4 shows a better distribution of amplitudes in the RUS spectrum, Fig. 5 driven by non-contact fields than those generated by the standard point contact drive. This is interesting because in terms of geological samples there is an advantage in being able to launch high frequency vibrations into rocks in an electrostatic non-contacting mode.

We have made a test using a sample of Fontainebleau sandstone, Fig. 6, which has single crystal quartz grains. Although the averaging process cancels the macroscopic strain there is still local strain between grains and field nonuniformity can be used to excite a smaller number of grains. This is an inherently low *Q* sample

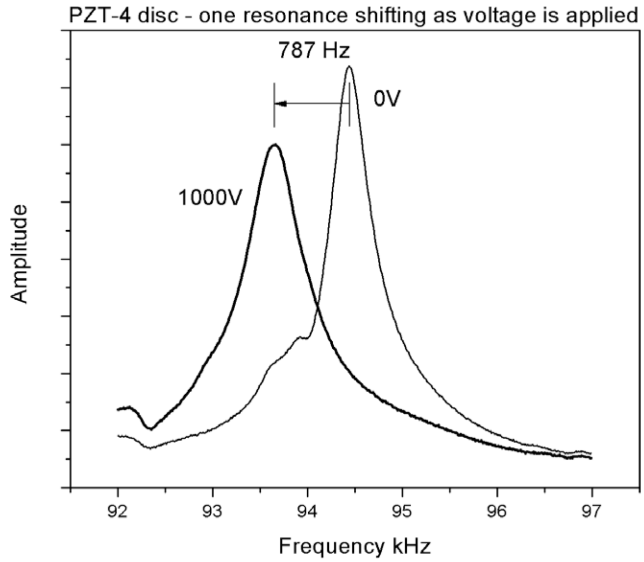

Fig. 8. The shift in resonance frequency in a poled thick PZT-4 disc by application of a DC voltage. The shift is dominantly due to the induced static strain.

but it is clear from Fig. 7 that several of the resonances generated by the point contact transducers are visible in the spectrum from the *E*-field exciter. The signal is very low as we might expect from the non-averaged strain, but the signal to noise is quite high and likely to contain much more information on the vibrations of the rock. We are working to improve the sample geometry and driving field strength.

Other modern dielectric materials are interesting as either transducer materials or as materials which can be elastically characterized [17] by RUS measurements. We have tested the response of a 25 mm diameter PZT-4 disc transducer by examining the shift of a resonance peak under the application of 1 kV across the disc, Fig. 8. The displacement of the peak corresponds to 0.78 Hz/V. Hertz-level displacements are within the resolution of this RUS measurement even though the *Q* of the peak is only ~150 and decreases to ~100 upon application of the voltage. An increase in dissipation is apparent by this broadening of the peak. The behavior is dependent on the mode but since RUS measures many modes in one sweep a, complete determination of some properties would be possible in a short time. Commercially available relaxor ferroelectrics like PMN and PMN-PT use the electrostrictive effect to provide strains almost comparable to piezoelectrics [18], but the mechanism of large electrostriction is still not well understood in many materials, opening opportunities for materials studies with RUS in this class of nanostructured materials.

5. Conclusions

The interaction of electric fields with material properties is an underexplored branch of measurement and research. Using acoustic techniques, particularly those using resonant amplification many of the tensor properties can be studied using small samples and lower voltages than with pulse-echo techniques. Novel dielectrics and their electroelastic interactions have an increasing share of new technologies, and may well spin off innovative transducer designs in the field of ultrasonics.

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