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Polarization Echoes and Long-Time Storage in Piezoelectric Powders

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Two- and three-pulse polarization echoes are detected in powders of mechanically resonant particles of piezoelectric materials. Under some conditions the decay time of the three-pulse echo can be of order one day or longer. A model for the echo formation and long decay time based upon the torque exerted on an oscillating dipole by an applied rf field is described.

The linear absorption and radiation of radio-frequency energy by electromechanical oscillations of piezoelectric particles has been known for some time.[1] Similar effects have been observed in particles of magnetoelastic materials.[2] Subsequently polarization echoes have been reported in magnetoelastic[3] and piezoelectric[4] powders. In polarization-echo experiments, as is also the case in spin echoes, rf pulses are applied to the powder samples at times $t=0$, τ, and T. The two-pulse echo, e_2, is radiated by the sample at $t=2\tau$ and the three-pulse echo, e_3 is radiated at $t=T+\tau$. The relaxation times T_2 and T_1 are defined by $e_2 \propto \exp(-2\tau/T_2)$ and $e_3 \propto \exp(-2\tau/T_2 - T/T_1)$. In piezoelectric powders T_2 and T_1 are typically 10^{-3} sec or less. However, recent experiments[5-8] have shown that the relaxation time T_1 can exceed days in some cases. Relaxation times of this magnitude must be attributed to some static or stored polarization property of the powder sample and cannot be associated with any dynamic behavior of the system.

In this Letter we report new experimental and theoretical results on the polarization-echo storage phenomenon in powders of mechanically resonant particles of piezoelectric materials. We have detected the storage effect in several piezoelectric materials at radio frequency (20–200 MHz) and in one material, ZnO, at X-band microwave frequencies (9 GHz). We propose a model to explain the mechanism of echo formation and the origin of the decay time, T_1, of the three-pulse or "stimulated" echo.

In our experiments the amplitude of the rf electric field pulses applied to the powder sample were of order 5×10^3 V/cm and the pulse widths were of order 10^{-6} sec. In strongly piezoelectric materials the echo signals are quite intense. For example in a 1-cm^3 sample of $LiNbO_3$ powder, peak radiated echo powers of order 10^{-1} W were detected on application of peak pulse powers of order 10^3 W. Application of a single rf pulse to a mechanically resonant sample causes the individual particles to oscillate or "ring" at their natural frequencies. This ringing is detected after each pulse as a somewhat irregular signal which decays approximately exponentially. This decay as well as the T_2 from the echo decay was found to be dependent upon particle size, frequency, temperature, particle packing density, and particle surface finish. In addition, two-pulse echoes were detected in powders of every piezoelectric material we studied, including natural and hydrothermally grown quartz, sand, CdS, CdTe, ZnO, ZnSe, GaAs, $BaTiO_3$, $LiNbO_3$, K_x-$Li_{1-x}NbO_3$, $LiTa_{0.8}Nb_{0.2}O_3$, Li_2GeO_3, $Gd_2(MoO_4)_3$, SbSI, Se, PLZT (lead-based, lanthanum-doped zirconate titanate) ceramic, $RbAg_4I_5$, and triglycine sulfate. Other workers have reported on additional materials.[4-7] In the absence of con-

tradictory evidence we conclude that polarization echoes can be formed in powders of all piezoelectric materials. T_2 is typically in the range $(1-100)\times 10^{-6}$ sec.

With regard to the three-pulse echo with long T_1, the principal experimental results can be summarized as follows: (i) Three-pulse echoes are detected at 4.2 K in almost all samples and in many samples at 300 K. In one material ($LiNbO_3$) no T_1 decay was observed over a period of several days at 300 K. (ii) The echo amplitude is frequency and particle-size dependent as has been pointed out previously. Our experiments were performed in the frequency range 10–100 MHz with particles whose diameters were in the 30–150-μm range, and at 9 GHz in submicron ZnO. The fundamental mechanical resonance frequency of a particle of diameter d is given by $\Omega \simeq \pi v/d$. For $v = 5\times 10^5$ cm/sec and $d = 50$ μm, $\Omega/2\pi \simeq 50$ MHz. All the particle-size and frequency results indicate that mechanical oscillations of individual particles are excited by the pulses and play an important role in the echo formation process. (iii) Repetitive application of a two-pulse sequence with the relative phase of the first two pulses held fixed caused the three-pulse echo amplitude, e_3, to integrate whenever T_1 exceeded the repetition period of the sequence. Sometimes several tens of thousands of sequences were required to integrate e_3 to its maximum value. In some cases echoes were detected above the noise only after integrating. (iv) Under those conditions for which long T_1's were observed, a sharp "rap" applied to the sample at $\tau < t < T$ destroyed the stored "pattern" formed by the first two pulses and no three-pulse echo was observed at $T+\tau$. On the other hand, in some cases a slight tapping of the samples during integration [(iii) above] increased the rate at which e_3 built up. (v) The polarization-echo amplitudes show a qualitative correlation with the magnitude of the electromechanical coupling coefficient of the piezoelectric materials.

Since echoes cannot be formed by a linear system, various nonlinear magnetoelastic,[3] electroacoustic,[4] or anharmonic[7] interactions have been postulated as sources of the polarization echoes observed in powders. In all models, including ours for the long-T_1 decay, it is assumed that the first applied pulse excites the particles into mechanical resonance with a linear damping time, T_2. The only previous interpretation[5] of the three-pulse echo decay which leads to long T_1's is based upon a charge redistribution model which is similar to the polarization-echo storage mechanism in single crystals of piezoelectric semiconductors.[9] We find no evidence that this mechanism is applicable to polarization echoes in piezoelectric powders. Our reasons for believing that the physical origin of polarization echoes in powders is different from that for polarization echoes in single crystals of piezoelectric semiconductors are that the latter process involves propagating elastic waves, is extremely sensitive to the defect chemistry of the material, and is quite sensitive to light and dc bias fields.[10] In powders the process involves standing elastic waves and is apparently insensitive to defect chemistry. Storage is observed in powders of materials for which none was observed in single crystals, and is found to be insensitive to light and only weakly dependent upon biasing dc fields.

We believe that the polarization-echo phenomenon with long-T_1 decays found in powders of mechanically resonant piezoelectric particles can be understood on the basis of the following model. We assume that the applied rf pulses excite the piezoelectric particles into mechanical oscillation at their natural frequency. (For purposes of simplicity we assume that there is at most one mode of each particle contained within the frequency bandwidth of the experiment.) Subsequent applied rf fields exert a torque on the particles determined by the vector product of the field with the electric dipole associated with the piezoelectric oscillation. This torque contains frequency components at both the sum, $\omega+\Omega$, and the difference, $\omega-\Omega$, of the applied field frequency, ω, and the natural frequency, Ω, of the particle. For purposes of echo formation we need consider only the resulting particle rotation at the difference frequency.

We simplify the excitation of a piezoelectric particle by an applied rf field to the following equation:

$$\ddot{S} + \frac{2}{T_2}\dot{S} + \Omega^2 S = \gamma\omega^2 \frac{e}{c} E(t)\cos\theta. \qquad (1)$$

Here, e is the piezoelectric coefficient, c the elastic constant, ω the driving frequency, $E(t)$ the applied field, γ a factor of order 1 arising from the boundary condition, θ the angle between the applied field and the piezoactive axis of the particle, and $Sa(x)$ the strain.[11] The electric dipole associated with the mechanical oscillation is $p = eS\int a(x)\,dx \equiv eS\bar{a}$ and is directed along the piezoelectric axis of the particle. The solution of Eq. (1) following the first rf pulse, $E_1(t)$, of frequency ω and duration Δ_1 is readily obtained to

give $p = p(t, \Omega)$, which is a dipole oscillating with frequency Ω and damping constant T_2. The component of $p(t, \Omega)$ along the direction of the applied field is $p_z(t, \Omega) = \cos\theta\, eS\bar{a}$ and for $t > \Delta_1$ is given by

$$p_z(t, \Omega) = -\frac{\gamma\bar{a}(\omega^2/c)e^2E_1T_2\cos^2\theta}{4\Omega}\exp(-t/T_2)e^{i\Omega t}\frac{\exp(f\Delta_1/T_2)-1}{f} + \text{c.c.}, \tag{2}$$

where $f = 1 + i(\omega - \Omega)T_2$, and we have neglected sum-frequency terms. For a sample consisting of many particles, the video response of the external electrical circuit to a single pulse is proportional to

$$R(t) = \langle|\textstyle\sum_\Omega p_z(t, \Omega)|\rangle, \tag{3}$$

where the angular brackets denote the time average over an rf cycle of the magnitude of the quantity enclosed. For a small ($\lesssim 10^5$) number of particles and therefore a small number of resonant frequencies, $R(t)$ appears as an irregular signal decaying approximately as T_2. This signal is the well-known piezoelectric ringing detected after an applied pulse[1] and results from the incomplete phase cancelation of the oscillations of the individual particles. As the number of particles is increased to the point at which the sum in Eq. (3) can be replaced by an integral over a continuous distribution of particle resonant frequencies, $R(t)$ becomes a smooth function decaying with the time constant T_2^*, where $(T_2^*)^{-1}$ is the width of the distribution. Numerical evaluations of Eq. (3) are in good qualitative agreement with the experimentally observed dependence of $R(t)$ on the number of particles. In a sample consisting of $\sim 10^{11}$ submicron particles of ZnO no ringing was detected.

The field of the second pulse, $E_2(t-\tau)$, acting on this dipole exerts a torque on the particle given by $|\vec{G}(t)| = |\vec{p}(t, \Omega) \times \vec{E}_2(t-\tau)| = E_2(t-\tau)eS(t, \Omega)\bar{a}\sin\theta$. Equating the rate of change of angular momentum to $\vec{G}(t)$, we have an equation of motion for θ:

$$\ddot{\theta} + \Gamma\dot{\theta} = I^{-1}\sin\theta E_2(t-\tau)p(t, \Omega), \tag{4}$$

where Γ is an angular damping factor which arises from electrical and mechanical interparticle interactions and I is the relevant moment of inertia of the particle. For times such that $(t-\tau)\Gamma \gg 1$, and with the initial condition $\theta = \theta_0$, we find $\theta = \theta_0 + \theta_\tau$, where

$$\theta_\tau(\Omega) = \frac{\gamma\bar{a}(\omega^2/c)e^2\sin\theta_0\cos\theta_0}{I8\Gamma\Omega}E_1E_2T_2^2\exp(-\tau/T_2) \times\left[i\left(\frac{\exp(f\Delta_1/T_2)-1}{f}\right)\left(\frac{\exp(-f\Delta_2/T_2)-1}{f}\right)e^{i\Omega\tau} + \text{c.c.}\right]. \tag{5}$$

Each particle has rotated through an angle θ_τ determined largely by the frequency Ω of that particle. Because the distribution of particle sizes leads to a distribution of natural frequencies, Ω, a pattern is formed with each particle having rotated through an angle $\theta_\tau(\Omega)$, dependent upon its natural frequency. This pattern remains stable as long as the individual particles are not disturbed from their new orientations, thus explaining the long T_1 and the effect of mechanical vibration in destroying the stored polarization.

Application at $t = T$ of a third pulse, $E_3(t-T)$, probes the pattern. Expanding the right-hand side of Eq. (1) to first order in θ_τ, the driving force, $F(t)$, may be written as

$$F(t) = \gamma eE_3(t-T)(\cos\theta_0 - \sin\theta_0\theta_\tau) = F_{\text{linear}} + F_{\text{nonlinear}}. \tag{6}$$

Solving Eq. (1) with the nonlinear driving force in Eq. (6) and calculating the component of the resulting dipole along the direction of the applied field, we obtain

$$p_z(t, \Omega) = \frac{(\gamma\bar{a}\,\omega^2/c)^2e^4}{I}\frac{\sin^2(2\theta_0)}{128\Gamma\Omega^2}E_1E_2E_3T_2^3\exp[-(t-T+\tau)/T_2] \times\left[i\left(\frac{\exp(f\Delta_1/T_2)-1}{f}\right)\left(\frac{\exp(-f\Delta_2/T_2)-1}{f}\right)\left(\frac{\exp(f^*\Delta_3/T_2)-1}{f^*}\right)e^{-i\Omega(t-T-\tau)} + \text{c.c.}\right], \tag{7}$$

where the terms in $e^{-i\Omega(t-T-\tau)}$ have been omitted and Δ_i is the width of the ith pulse.

The stimulated echo response of the powder sample is obtained by substituting this result into Eq. (3). Again, in the case of a finite number of particles, the echo at $t = T + \tau$ is superimposed on the irregular ringing of the sample resulting from incomplete phase cancelation of the oscillations of the in-

dividual particles. As expected, no echo can be detected for a very small number of particles. In the continuum limit the echo shape given by Eq. (3) is the same as the analogous spin echo.

The model outlined here to explain the long T_1's is based entirely on the physical rotation of the individual particles as a consequence of the torque exerted on an oscillating dipole by an applied rf field. It is important to note that the sample polarization which gives rise to the echo is the total pattern of individual particle rotations. The pattern can be probed many times to create an echo, as long as the field of the probing pulse does not exceed the fields used to create the pattern. In conclusion we remark that the only particle-particle interactions which have been included in the model are those giving rise to the angular damping constant Γ of Eq. (2). Interparticle coupling may be important in determining T_2[7] and T_1.

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Phonon-Assisted Energy Transport in Inhomogeneously Broadened Systems*

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Recent experiments have demonstrated Anderson localization in inhomogeneously broadened paramagnetic spin systems. We examine two-phonon processes which can frequency shift the individual spin packets, and thereby allow energy transfer to take place. We make specific application to ruby, and show that the dominant phonon-induced energy-transfer rate is directly proportional to the (spin-nonflip) $\bar{E} \rightarrow 2\bar{A}$ rate [varying as $\exp(-42/T)$], and inversely proportional to the square of the energy mismatch of the participating spin packets.

Recently, Hsu and Powell[1] and, independently, Koo, Walker, and Geschwind[2] have reported evidence of Anderson localization[3] in inhomogeneously broadened optical transitions in paramagnetic crystals (the former in $CaWO_4$:Sm; the latter in Al_2O_3:Cr, ruby). Also, Flach *et al.*[4] have reported evidence of phonon-assisted energy transfer within an inhomogeneously broadened optical line. The purpose of this Letter is to calculate the two-phonon-assisted contribution to energy transfer in inhomogeneously broadened spin systems. Because of the wealth of information available for ruby, we shall make direct application of our results to that system, though our approach is considerably more general. Our findings are that, for the case of ruby, (1) there is no significant