Amplification of polarization echo signals in lithium niobate crystals activated with iron group ions

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A qualitative description is given of the surface formation of a discrete echo excited by microwave pulses at the moment of reflection of ballistic hypersonic pulses from the faces of an $LiNbO_3$:Fe crystal illuminated with high-intensity pulses of coherent light. Doping of $LiNbO_3$ with nickel ions enhanced (by a factor of ~1000) the polarization echo at a frequency of 9.5 GHz; this echo was suppressed by a static magnetic field. Measurements were made of the relaxation times of the echo signals in various ferroelectrics.

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The polarization echo discovered by Kopvillem *et al.*[1] is a coherent electromagnetic response of a ferroelectric (or piezoelectric) crystal to the action of two pulses of the electric component of a microwave field in the case when the durations of the exciting pulses Δt_1 and Δt_2, and the interval between them τ, are less than the characteristic relaxation times. At ~10 GHz this nonresonance effect is observed at helium temperatures.

The formation of the polarization echo signals may be described by nonlinear equations of the theory of elasticity.[2] The theoretical analyses of the electroacoustic echo in piezoelectric powders[2,3] have been concerned with the bulk excitation of the echo signals, when measurements can be made by varying continuously the interval τ between the excitation pulses. However, we shall show that the same equations describe qualitatively also the surface formation of the discrete echo signals observed only for fixed intervals between the excitation pulses.[4]

Expansion of the energy of a piezoelectric material $\mathcal{E}(\mathbf{E}, \mathbf{e})$ as a series in powers of an external electric field **E** and components of the strain tensor **e** has the form

$$\mathcal{E}(\mathbf{E}, \mathbf{e}) = \mathcal{E}_0 + {}^1/_2 \mathbf{C}\mathbf{e}^2 + \mathbf{d}\mathbf{e}\mathbf{E} - {}^1/_2 \chi \mathbf{E}^2 + {}^1/_2 \mathbf{f}\mathbf{e}^2\mathbf{E}^2 + \ldots, \tag{1}$$

where **C** is the tensor of the elastic constants, χ is the susceptibility, **d** is the tensor of the piezoelectric constants; out of the many possible anharmonic terms, only the one needed in a qualitative description of the echo formation process is included explicitly.

We shall assume that a sample in the form of a rod of a unit cross section and of length l with its generator along the x axis is acted upon by an alternating electric field $E_x(t) = E_1(t) + E_2(t)$, where

$$E_i(t) = E_i \sin \omega t [\theta(t - \tau(i-1)) - \theta(t - \tau(i-1) - \Delta t_i)], \tag{2}$$

which excites longitudinal acoustic vibrations $u_x(x, t)$ accompanied by the strain $e_{xx} = \partial u_x / \partial x$. The equation of motion becomes

$$\frac{\partial^2 u_x}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2 u_x}{\partial t^2} = -\frac{1}{C}\frac{\partial}{\partial x}[E_x d + E_x^2 e_{xx} f + \ldots]\varphi(x), \tag{3}$$

where v is the velocity of sound and the factor $\varphi(x) = \theta(x) - \theta(x - l)$ governs the boundary conditions. The solution of Eq. (3) in the zeroth approximation (only the term proportional to the piezoelectric modulus d remains on the right-hand side) describes acoustic vibrations traveling from the boundaries of the rod along the x axis; in particular, at the point $x = 0$ the first microwave pulse excites a train of waves which occupy a volume $\Delta x = v\Delta t_1$ in the rod and create an alternating strain

$$\frac{\partial u_{x1}}{\partial x} = \frac{E_1 d}{2C} \sin\left[\omega\left(t - \frac{x}{v}\right)\right]\left[\theta\left(t - \frac{x}{v}\right) - \theta\left(t - \frac{x}{v} - \Delta t_1\right)\right]. \tag{4}$$

We shall be interested in the nonlinear response of the rod to the pulses $E_1(t)$ and $E_2(t)$ at times $t > \tau + \Delta t_2$; we shall assume that $d = 0$ in Eq. (3) and, in the first approximation, we shall replace e_{xx} on the right-hand side of Eq. (4). The equation of motion then becomes

$$\frac{\partial^2 u_x}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2 u_x}{\partial t^2} = A_v(x, t) + A_s(x, t), \tag{5}$$

where

$$A_v(x, t) = -\frac{f}{C} E_2^2(t)\varphi(x)\frac{\partial^2 u_{x1}}{\partial x^2}, \tag{6}$$

$$A_s(x, t) = \frac{f}{C} E_2^2(t)\delta(x - l)\frac{\partial u_{x1}}{\partial x}; \tag{7}$$

for brevity, the right-hand side of the linear inhomogeneous equation (5) does not include the terms which are important in discussing the waves traveling from the point $x = l$.

The effective driving force $A_v(x, t)$, due to the action of the microwave pulse $E_2(t)$ on the traveling acoustic wave at an arbitrary point inside the sample, generates the echo signals considered earlier by Fedders and Lu.[2] The corresponding solution of Eq. (5), describing a wave traveling in the opposite direction, is

$$u_x(x, t) \sim \frac{fd}{16C^2} E_1 E_2^2 v \cos\left[\omega\left(t + \frac{x}{v}\right)\right] F(x, t). \tag{8}$$

The form of the echo signal induced on the $x = 0$ sur-

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face as a result of phase matching of the vibrations excited by the first pulse is governed by the function $F(0,t)$ which differs from zero in the interval $\Delta t_1 + 2\Delta t_2$ near the point $t = 2\tau$ and has the maximum value defined by $\min(\Delta t_1, 2\Delta t_2)$. The echo signals described by Eq. (8) can be observed in samples with any shape of the surface; in the experiments on plane-parallel samples (surface finish smooth to within the wavelength of sound), the oscillograms should reveal not only the echo but also microwave signals due to ballistic hypersonic pulses, separated by the time interval l/v and generated on the suitably treated ends of the sample. In accordance with the theoretically predicted[2] formation of the echo signals throughout the insonated volume of the sample, the experiments reveal an increase in the intensity of the signals on increase in the amount of matter.

The term $A_s(x,t)$ in Eq. (5), not included earlier, creates vibrations

$$u_x(x,t) \sim \frac{fd}{16C^2} E_1 E_2^2 \frac{v}{\omega} \cos\left[\omega\left(t + \frac{x-2l}{v}\right)\right] \Psi(x,t), \qquad (9)$$

which travel from the $x = l$ face and generate an additional echo signal on the opposite face $x = 0$. The shape of this signal is given by the function

$$\Psi(x,t) = \theta\left(t - \frac{x-l}{v} - \max\left(\tau + \Delta t_2, \frac{l}{v} + \Delta t_1\right)\right) + \theta\left(t - \frac{x-l}{v} - \max\left(\tau, \frac{l}{v}\right)\right) - \theta\left(t - \frac{x-l}{v} - \max\left(\tau + \Delta t_2, \frac{l}{v}\right)\right) - \theta\left(t - \frac{x-l}{v} - \max\left(\tau, \frac{l}{v} + \Delta t_1\right)\right), \qquad (10)$$

which differs from zero on the $x = 0$ face only for certain values of the interval τ between the microwave pulses:

$$l/v - \Delta t_2 \leqslant \tau \leqslant l/v + \Delta t_1. \qquad (11)$$

This condition follows from the need for the overlap of an acoustic ballistic pulse at Δt_1 duration with the second microwave pulse of Δt_2 duration on the $x = l$ face. The echo signal is excited on the $x = 0$ face at moments $t = 2l/v + T$, where the interval T, equal to the overlap time of the acoustic and microwave pulses at the point $x = l$, is governed by the condition $\Psi(0,t) \neq 0$.

The echo which has the above properties is called discrete in our earlier paper.[4] The proposed theory of the discrete echo is easily generalized to the case of interaction with an acoustic pulse after it makes n passes through the crystal: it is sufficient to replace l with nl in Eqs. (9)–(11). A comparison of Eqs. (8) and (9) shows that the ratio of the amplitudes of the polarization echo formed in the bulk of the crystal and the discrete echo is $\sim\omega\Delta t_1$, so that under the conditions in our experiments ($\omega \sim 10$ GHz, $\Delta t_1 \sim 4 \times 10^{-8}$ sec) the discrete echo signals should be three orders of magnitude weaker than the polarization echo signals. Allowance for other nonlinear terms in the expansion (1) of the bulk energy density in the crystal (in particular, an analysis of the anharmonicity of the vibrations) does not alter this estimate of the ratio of the echo signal amplitudes. However, since the discrete echo is formed on the surface of the sample, it can be amplified effectively by altering the surface dielectric and other properties of a crystal. The required amplification was achieved in our case by laser illumination of activated niobium crystals of the type used in holographic storage.[4]

Measurements of the polarization echo were carried out by us on single-domain $LiNbO_3$ crystals at 1.8–4.2 °K at a frequency 9.4 GHz. Crystals of $2 \times 5 \times 10$ mm dimensions were placed in a microwave cell, whose construction enables us to excite hypersonic vibrations traveling toward one another from the two plane-parallel suitably treated faces of the sample. The action of a pair of microwave pulses of ~40 nsec duration with an arbitrary interval (not exceeding the relaxation time $T_r \sim 10^{-6}$ sec) produced weak single polarization echo signals, whose intensity was independent of the treatment of the faces of the sample. A comparison of the changes in the intensities of the echo signals and decay constants of the ballistic acoustic pulses in various crystals indicated that an increase in the degree of imperfection of the structure resulted in enhancement of the polarization echo signals clearly because of local enhancement of the nonlinear parameters of the crystal lattice.

The high-intensity discrete echo signals, which appeared for fixed values of the interval equal to, or multiple of, the transit time of hypersound through the sample ($\tau_n = nl/v$) were observed for crystals with optically flat and parallel faces, perpendicular to the x axis, and containing ~0.03 wt.% Fe; these crystals were illuminated with high-intensity (50 MW/cm^2) ~20 nsec coherent light pulses of ~0.53 μ wavelength.

The optical inhomogeneity of the lithium niobate lattice induced by the laser beam was attributed to a localized change in the refractive index.[5] The optical sensitivity of the crystals increased strongly on doping with the Fe^{2+} ions, which acted as donors under photoexcitation conditions. The distribution of photoelectrons between traps around the illuminated region defined the area with modified dielectric characteristics. When the whole sample was illuminated, photoelectrons diffused toward the surface where the trap concentration was usually higher than in the bulk of the crystal. Thus, the greatest changes in the lattice characteristics occurred in the surface layer, which played the dominant role in the formation of the discrete echo signals.

In the illuminated $LiNbO_3$:Fe crystals the intensities of the ballistic hypersonic pulses excited by single microwave pulses and the intensities of the polarization echo signals were practically the same as before illumination. The discrete echo signals were observed at moments $2\tau_n$ only in the illuminated samples; their appearance was manifested by a sudden increase in the intensity of the recorded microwave pulses above the background of the combined signals representing the hypersonic pulses and polarization echo, and also by the appearance of secondary echo signals. Variation of the delay τ in one or other direction by an amount greater than the overlap time of the acoustic and second microwave pulses on the faces of a sample destroyed the echo completely, which reappeared after the next interval $\tau_{n\pm1}$. The relaxation time of the discrete echo signals was of the same order of magnitude as the relaxation time of the conventional polarization echo.

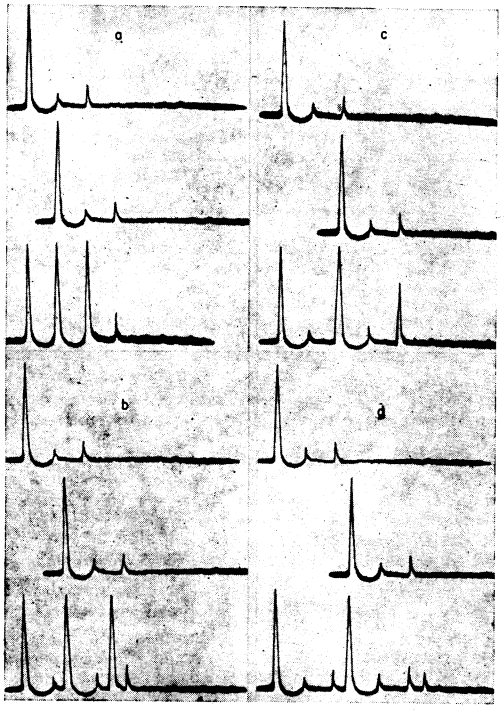

FIG. 1. Oscillograms of discrete echo signals after delay times τ_2 (a), τ_3 (b), τ_4 (c), and τ_5 (d). In each case the response pattern is given to single microwave pulses and to pairs of pulses.

Oscillograms of single microwave pulses accompanied by acoustic pulses and discrete echo signals at intervals τ_n with $n=2$, 3, 4, and 5 are shown in Fig. 1. We can see that the echo signals at moments τ_{2n} are considerably greater than the total response of the microwave cell to the acoustic pulses reflected from the ends of the rod.

The common nature of the mechanisms responsible for the amplification of the discrete echo signals and recording of optical holograms in $LiNbO_3$:Fe crystals was indicated by a complete analogy between the recording (storage) sensitivity and the intensity of the discrete echo signals, considered as a function of the heat treatment (annealing) of the crystals and of the concentration of the iron impurity ions. Heating of the illuminated samples and their prolonged storage erased the recorded information and reduced the discrete echo signals. In the case of samples which were not doped with iron, the discrete echo was observed only after a considerable increase of the illumination dose compared with the activated sample.

Numerical estimates[3] indicated that the amplitude of the polarization echo at the frequency of the exciting pulses should be governed primarily by the fourth-order lattice anharmonicity [terms of the $\mathbf{g}\cdot\mathbf{e}^4/4!$ in the expansion (1)]. The eighth-rank tensor $\mathbf{g}$ plays the same role in the nonlinear acoustic phenomena as the electric susceptibility (fourth-rank tensor) in nonlinear optics. The echo signal is proportional to the real part of the complex nonlinear phonon susceptibility $g(-\omega, -\omega, -\omega, \omega)$. The terms of the quantum-mechanical expression for the nonlinear susceptibility $g(\omega_4, \omega_3, \omega_2, \omega_1)$, representing the polarization of a medium at the frequency $\omega_4=\omega_3+\omega_2+\omega_1$, contains factors of the $(\omega_{\alpha\beta}\pm\omega_i)^{-1}$ and $(\omega_{\alpha\beta}\pm\omega_i\pm\omega_j)^{-1}$ types, where $\hbar\omega_{\alpha\beta}$ is the difference between the energies of the electron states of the system which are mixed by the electron–phonon interaction operator.[6] We can therefore expect that doping of piezoelectric crystals with paramagnetic ions characterized by a sufficiently strong electron–phonon interaction will make it possible to control the polarization echo signals by a static magnetic field which alters the ratio of the Zeeman splittings and microwave pulse harmonics [resonant amplification of the echo signals is possible at $\omega_{\alpha\beta}=0$ (for ions with an even number of electrons), ω and 2ω].

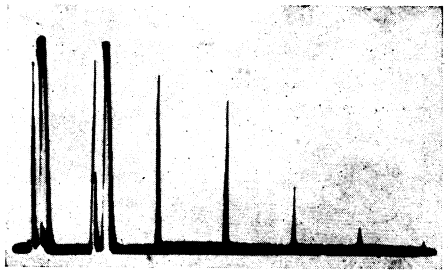

FIG. 2. Polarization echo in an $LiNbO_3$:Ni crystal. The oscillogram shows the microwave and echo pulses; the high intensity of the main signal resulted in the appearance of secondary echo signals.

We determined the polarization echo signals excited by microwave pulses of up to several kilowatt power at a frequency of 9.5 GHz in lithium niobate crystals activated with chromium, iron, copper, cobalt, and nickel ions. A considerable change in the signal amplitude (an increase by a factor of about 1000) compared with a single-domain reference sample free of impurities was observed only for crystals containing nickel ions (Fig. 2).

The Ni^{2+} ions can, like Cr^{3+},[5] replace Li^+ or Nb^{5+} in oxygen octahedra with trigonal distortion along the optica axis c of a crystal. The absorption spectrum of an $LiNbO_3$:Ni crystal exhibited three wide bands with maxima at 8×10^3, 13×10^3, and 23×10^3 cm^{-1}, which could be attributed to the $^3A_2\rightarrow{}^3T_2$, $^3T_1(^3F)$, and $^3T_1(^3P)$ transitions, respectively. The effective spin Hamiltonian of the ground state $^3A_2$ had the form (x axis parallel to c axis)

$$\mathcal{H}=D(S_z^2-{}^1/_3S(S+1))+g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y).$$

The spin triplet ($S=1$) was split by the trigonal component of the crystal field into a singlet and a doublet; the $S_z=\pm1$ doublet split linearly with the field H_z and in a weak field $\mathbf{H}\perp c$ the difference between the energies of the doublet and singlet sublevels was proportional to $(g_\perp\beta H)^2/D$.

In the ESR spectra of an $LiNbO_3$:Ni crystal at 2–4.2 °K a pair of two wide lines with $g_\parallel$ equal to 4.48 and 8.62 ($g_\parallel\beta H_z=\hbar\omega$) was observed at frequencies 9.5, 36.5, and 70 GHz; these lines rapidly broadened and shifted toward higher fields when the orientation of the

magnetic field was varied from H||c to H$\perp c$. It was not possible to establish definitely the origin of these lines but the transitions between the Zeeman sublevels of the Ni^{2+} ion were not observed clearly because of a strong inhomogeneous (deformation) and relaxation broadening. In weak fields ($H < 400$ Oe) the ESR spectrum at the echo-measurement frequency 9.5 GHz exhibited a wide absorption line edge and in the same range of magnetic fields a polarization echo of anomalous intensity was observed. When the cell containing an $LiNbO_3$:Ni crystal located at an antinode of the electric component of the microwave field was subjected to a static magnetic field H$\parallel c$, the echo signal decreased rapidly on increase of H and became comparable with the signal from a reference sample in $H > 1600$ Oe. In the H$\perp c$ field we observed a less steep dependence of the echo amplitude on the value of H. One could assume that the high signal intensity was due to the excitation of the resonance spin echo in zero magnetic field ($D \approx \hbar\omega$) but this interpretation of the effect was not in agreement with the absence of any changes in the echo signal in resonance fields at the ESR line frequency or in the nature of the absorption of hypersound; moreover, it did not agree with the measured relaxation times. It was more likely that the ESR line in zero field corresponded to two-quantum transitions and the amplification of the polarization echo was due to the closeness of the second microwave harmonic and the initial splitting of the levels of the Ni^{2+} ions ($D \approx 2\hbar\omega$).

The results of our measurements of the relaxation times of the echo signals in various ferroelectric crystals are presented in Table I. At the lowest power of the exciting microwave pulses sufficient to produce the echo, the value of T_2 for $LiNbO_3$:Ni was of the order of 7.5 μsec. As the microwave power was increased, we observed that samples with the treated faces perpendicular to the c axis exhibited generation of hypersound (ballistic acoustic pulses were detected as a result of reflections from the plane-parallel ends of the crystal) and the relaxation times lengthened to 20 μsec. In a magnetic field of $H > 1000$ Oe the relaxation time was 3 and 15 μsec, respectively, for low and high powers of the exciting microwave pulses. The lengthening of T_2 exhibited by the activated samples on increase of the acoustic power was probably associated with the resonant nonlinear phonon trapping.[7]

We shall conclude by pointing out that the observation of intense polarization echo signals in $LiNbO_3$:Ni crystals have made these crystals very valuable in the search for other nonlinear acoustic effects, particularly phonon self-focusing. The possibility of microwave readout of optically recorded information in $LiNbO_3$:Fe crystals may be useful in technical applications.

TABLE I. Relaxation times of polarization echo in ferroelectric single crystals measured by three-pulse (stimulated echo, T_1) and two-pulse (T_2) methods and deduced from dependences of signals on repetition period of excitation pulses (T_x).

Substance	T_1, 10^{-3} sec	T_2, 10^{-6} sec	T_x, 10^{-3} sec
$LiNbO_3$ *	0.02	1.2	1.7
$LiNbO_3$:Ni ***	–	see text	–
$LiTaO_3$ ***	0.01	~1	1.4
KDP (KH_2PO_4) ***	0.004	1.0	0.3
DKDP (KD_2PO_4) **	–	~1	1.1
RDP (RbH_2PO_4) **	–	1.6	2.5
DRDP (RbD_2PO_4) *	–	1.5	2.3
CDA (CsH_2AsO_4) **	–	~1	3.3
DCDA (CsD_2AsO_4) *	–	~1	3.0
RDA (RbH_2AsO_4) **	–	6.4	4.0
$Ba_2NaNb_5O_{15}$ **	–	0.2	1.0
SbSI **	–	0.4	1.0

*Very weak echo signals, **weak signals, ***strong signals.

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