Polarization echo in piezoelectric powders

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The mathematical formalism that describes the echo in a system of anharmonic oscillators and was previously employed in the theory of cyclotron echo in a plasma is used here to describe polarization echo in piezoelectric powders. In addition to the known result for a two-pulse echo, account is taken of the damping of the oscillations, of the finite duration and width of the frequency spectrum of the exciting pulses; an expression describing the echo signals following three-pulse excitation of the sample is obtained. The anharmonicity of the oscillator is assumed to be due to dislocations in the crystal, and this makes it possible to explain the prolonged memory times T_1. The experimental dependences of the polarization-echo signals and of the responses from individual powder particles are presented. The results of the theory are corroborated by all the known experimental data.

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1. INTRODUCTION

A phenomenon analogous to spin echo in NMR has been observed in various powdered structures: piezoelectrics, ferromagnets, diamagnetic metals, and paramagnetic compounds, and has been predicted for anisotropic dielectrics. A general description of these phenomena is apparently provided by an orientation model, [1–4] according to which the ensemble of excited oscillators (powder particles) forms a three-dimensional lattice of dipoles oriented in a definite manner, and this lattice contains information on the frequency, phase, and parameters of the exciting pulses. This model leads also to a long-duration (even infinite) memory of the stimulated echo, but cannot explain a fact revealed by us, that the memory is preserved after the sample is jarred or even resifted; nor can it explain the usually observed continuous spectrum of the finite values of the time T_1.

Other models devoted concretely to polarization echo in piezoelectric powders regard the sample as an ensemble of piezoelectric resonators (oscillators) with nonlinearities that are specified in one manner or another. Thus, in[5–7], getting around the difficulty of analytically solving the nonlinear oscillation equation, the authors solve the problem in a linear approximation and subsequently take into account the electro-elastic or elastic nonlinear effects of elasticity theory. To be sure, the solution of the nonlinear equation is described in[8], where it is shown, as stated by the authors, that the position and the shape of the echo signal do not depend on the manner in which the nonlinearity is taken into account. The obtained solutions describe the instants of the appearance of the echo signals and a number of their parameters and relationships: the shape and width, the dependence of the amplitude on the intensity and duration of the pulses and on the frequency of the field. This analysis should lead to echo signals at combination frequencies (as is in fact mentioned in[5]), but no such signals have been observed. In addition, the effects of damping and relaxation have not always been taken into account.

The interaction of a system of oscillators with an external field is described by Kuidersma *et al.*[9] by a nonlinear Hamiltonian, and the equation of motion is represented in the form of pseudo-Bloch equations. The solution, however, describes only the fact that an echo signal appears.

A number of workers[7,10,11] use for a qualitative explanation of the nature of the long-time memory of stimulated echo a model wherein the electrons are redistributed among the traps by a constant inhomogeneous electric field; this model was proposed in[12] to explain a similar phenomenon in CdS crystals. It is noted in[2], however, that this model is valid for elastic waves propagating in extended crystals and leads to a substantial dependence of the memory on the chemical defects of the lattice and on the illumination of the sample, something not observed when elastic oscillations of the standing-wave type are excited in powdered piezoelectrics.

In the present paper we use and develop Gould's oscillator model[13] previously proposed for the description of cyclotron echo in a plasma; the nonlinearity is the dependence of the particle oscillation frequency on the oscillation energy. The physical nature of the nonlinearity, according to our assumption, is due to dislocations in the crystal and it is this "intrinsic" content of the nonlinearity that distinguishes our mode from the orientational mode, and possibly supplements it, although it can explain independently also the long-time memory. Both the known and the additionally performed experiments confirm the premises and the principal results of the theory.

2. THEORY

A. Action of one pulse

A powdered sample can be regarded as an ensemble of almost identical particles—piezoelectric resonators with small damping, which interact weakly with one another and whose natural frequencies have a broad distribution spectrum. Each particle experiences the action of an identical radiofrequency field, so that the polarization of the sample is calculated by adding the elementary moments of the individual particles.

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The exciting pulsed radiofrequency field

$$E(t)=\begin{cases} E_0\cos(\omega_0 t+\varphi), & 0\leqslant t\leqslant\Delta t \\ 0, & t<0,\ t>\Delta t \end{cases}$$

has a frequency spectrum in the form $(\frac{1}{2}\omega'\Delta t)^{-1} \times \sin\frac{1}{2}\omega'_0\Delta t$, where $\omega'_0=\omega_0-\omega$. Inasmuch as in experiment we always have $\Delta t\ll T_2$, where T_2^{-1} is the damping parameter of the oscillating system (the particle), the width of the frequency spectrum of the pulse is much larger than the width of the resonance curve of the system, and it can be assumed that each particle is excited by the RF field under resonance conditions.

The equation of motion for the deformation of the particle is

$$\ddot{x}+\frac{2}{T_2}\dot{x}+\omega^2 x=\omega_0^2\gamma\frac{e}{c}\cos\theta E_0\cos(\omega_0 t+\varphi),$$

where e is the piezoelectric modulus, c is the elastic constant, θ is the angle between the direction of the field and the piezoelectric axis, and γ is a factor on the order of unity, which takes into account the boundary conditions.

After the end of the pulse, the oscillator oscillates at its natural frequency ω and undergoes a damping T_2^{-1}, while the solution for the polarization $p=e\chi$, in a coordinate system rotating with frequency ω_0, is

$$p(t)=A\cos^2\theta\exp\left(-\frac{t-\Delta t}{T_2}\right)\exp\{i[\omega'(t-\Delta t)+\varphi]\}, \quad (1)$$

where

$$A=\gamma\frac{e^2}{c}E_0\omega_0 T_2\frac{\sin(\omega'\Delta t/2)}{\omega'\Delta t/2}\left[1-\exp\left(-\frac{\Delta t}{T_2}\right)\right]. \quad (2)$$

The polarization of a sample consisting of N piezoactive particles is

$$P(t)=\int_{-\infty}^{\infty}A\exp\left(-\frac{t-\Delta t}{T_2}\right)G(\omega')\exp\{i[\omega'(t-\Delta t)+\varphi]\}d\omega',$$

where $G(\omega')$ is a normalized distribution function of the natural frequencies of the oscillators,

$$\int_{-\infty}^{\infty}G(\omega')d\omega'=N,\quad \overline{\cos^2\theta}=\frac{1}{2}.$$

B. Two-pulse echo

Following the oscillator model,[12] we can assume that the appearance of the echo signals in the system of piezoresonators is due to the dependence of the natural frequency of the particle on the energy of its oscillations, and take into account nonlinearities of two types:

a) Monotonic dependence

$$\omega(\mathscr{E})=\omega'+b\mathscr{E},\quad b=\frac{\partial\omega'}{\partial\mathscr{E}}=\left(\gamma\frac{e^2}{c}\omega_0 T_2\right)^{-2}b_E, \quad (3)$$

where $\mathscr{E}$ is the increment of the oscillation energy ($\sim A^2$) and $b_E=\partial\omega'/\partial(E_0^2)$.

b) Jumplike shift of the frequency outside the limits of the spectrum of the exciting pulse. Assuming that the number of such shifts is proportional to the energy of the oscillations and to the duration of the external action, the probability that there is no jump is

$$W=\exp(-a\mathscr{E}\Delta t). \quad (4)$$

It is obvious that this mechanism is effective only at large amplitudes of the external field.

Under these assumptions we can use the mathematical formalism of[13], but in contrast to the latter, the conditions of the experiment call for allowance for the damping of the oscillations, for the finite duration and width of the frequency spectrum of the exciting pulses.

Thus, two RF pulses with an interval $\tau<T_2$ and with parameters E_i, Δt_i, and φ_i are applied to the system (i is the number of the pulse, $\varphi_1=0$). The first pulse excites damped oscillations of the oscillators in accordance with (1), and the nonlinear interaction of the pulse with the system cannot make a noticeable contribution to the formation of the echo signal; it will therefore be disregarded henceforth, i.e., the natural frequency of the oscillator is regarded as constant and $W'=1$. By the end of the second pulse, the oscillation energy of the oscillator becomes equal to

$$\mathscr{E}_{1,2}=A_1^2\exp\left(\frac{-2\tau}{T_2}\right)+2A_1A_2\exp\left(-\frac{\tau}{T_2}\right)\cos[\omega'(\tau-\Delta t_1+\Delta t_2)-\varphi_2]+A_2^2, \quad (5)$$

where $\omega'(\tau-\Delta t_1+\Delta t_2)$ is the phase advance of the free oscillations excited by the first pulse by the time the second pulse has terminated. Here and below, we disregard in the exponentially damped factors the pulse durations, since $\Delta t\ll\tau$, but the quantity $\omega'\Delta t$ is finite. This energy determines the natural frequency $\omega''=\omega'+b\mathscr{E}_{1,2}$ of the oscillator and the probability $W''=\exp(-a\mathscr{E}_{1,2}\Delta t_2)$ of conserving the resonance conditions after the second pulse.

The polarization of the sample is

$$P(t)=\frac{1}{2}\int_{-\infty}^{\infty}\left\{A_1\exp\left(-\frac{\tau}{T_2}\right)\exp[i\omega'(\tau-\Delta t_1+\Delta t_2)]\right.$$

$$\left.+A_2\exp i\varphi_2\right\}\exp\left(-\frac{t-\tau}{T_2}\right)\exp[i\omega''(t-\tau-\Delta t_2)]W''G(\omega')d\omega'. \quad (6)$$

Substituting the quantities ω'', W'', and $\mathscr{E}_{1,2}$ in (6) and using a series expansion in analogy with[13], we can ultimately write

$$P(t)=\frac{1}{2}\int_{-\infty}^{\infty}\exp[iO(\beta)-O(\alpha)]\exp\left(-\frac{t-\tau}{T_2}\right)$$

$$\times\sum_{n=-\infty}^{\infty}(-i)^n\left[iA_1\exp\left(-\frac{\tau}{T_2}\right)J_{n+1}(\beta+i\alpha)+A_2J_n(\beta+i\alpha)\exp i\varphi_2\right]$$

$$\times\exp(in\varphi_2)\exp\{i\omega'[t-(n+1)\tau+n\Delta t_1-(n+1)\Delta t_2]\}G(\omega')d\omega', \quad (7)$$

where $\alpha=2A_1A_2\exp(-\tau/T_2)a\Delta t_2$, $\beta=2A_1A_2\exp(-\tau/T_2)\times b(t-\tau-\Delta t_2)$, $O(\alpha)$ and $O(\beta)$ are of the order of α and β, respectively. Judging from the last time-dependent factor, the derived expression describes the regular echo responses at instants of time close to $(n+1)\tau$, with $n=0$ corresponding to the response immediately after the second pulse, and $n=1, 2, \ldots$ corresponding to the first, second, etc., echo signals.

In the approximation where the amplitudes of the exciting pulses are small, i.e., when $\beta^2 \ll 1$, $\alpha=0$, and only the first term of the series expansion of $J_n(\beta)$ differ from zero, each term of the sum describing the echo at the instant $(n+1)\tau$ is given by

$$P_n((n+1)\tau)\approx\frac{1}{2}\int_{-\infty}^{\infty}(-i)^n A_1{}^n A_2^{n+1}(bn\tau)^n\frac{1}{n!}\exp\left(-\frac{2n\tau}{T_2}\right)$$
$$\times\exp[i(n+1)\varphi_2]\exp\{i\omega'[t-(n+1)\tau+n\Delta t_1-(n+1)\Delta t_2]\}G(\omega')d\omega', \quad (8)$$

or in final form, for the first two-pulse echo,

$$P_1(2\tau)\approx\frac{Ne^2}{2\sigma c}\gamma\omega_0 T_2 E_1 E_2{}^2\left[1-\exp\left(-\frac{\Delta t_1}{T_2}\right)\right]$$
$$\times\left[1-\exp\left(-\frac{\Delta t_2}{T_2}\right)\right]^2 b_E\tau\exp\left(-\frac{2\tau}{T_2}\right)\exp\left[i\left(2\varphi_2-\frac{\pi}{2}\right)\right]g(t,\Delta t). \quad (9)$$

The factor N/σ has appeared here as a result of the integration of the distribution function, inasmuch as for a large ensemble of particles their frequency distribution can be assumed to be close to uniform within a region σ that is much broader than the momentum spectrum. Thus, the shape of the echo signal is determined entirely by the durations of the exciting pulses and takes the form

$$g(t,\Delta t)=\frac{8}{\Delta t_1\Delta t_2{}^2}\int_{-\infty}^{\infty}\frac{\sin(\omega'\Delta t_1/2)\sin^2(\omega'\Delta t_2/2)}{\omega'^3}$$
$$\times\exp[i\omega'(t-2\tau+\Delta t_1-2\Delta t_2)]d\omega'. \quad (10)$$

Without presenting the cumbersome expression for the integral, we can note that the signal has a symmetric shape with a maximum displaced from the instant 2τ by an amount $-\Delta t_1+2\Delta t_2$; the amplitude of the signal is proportional (apart from the exponential factors in (9)) to

$$g(\Delta t)=\frac{2\pi}{\Delta t_2}\left(1-\frac{\Delta t_1}{4\Delta t_2}\right),\quad \Delta t_1<2\Delta t_2,$$
$$g(\Delta t)=2\pi/\Delta t_1,\quad \Delta t_1>2\Delta t_2; \quad (11)$$

the width of the echo at the base is $\Delta t_1+2\Delta t_2$.

C. Three-pulse echo

In addition to the first two pulses, a third pulse is applied to the system at the instant τ_1, with parameters E_3 and Δt_3, and with phase shifts φ_2 between the first and second pulse and $\varphi_3=0$ between the first and the third pulses.

Calculations similar to those used for the two-pulse echo, neglecting the small terms ($\beta^2 \ll 1$, $\alpha=0$) yield

$$P(t)\sim\sum_l\sum_m\sum_n\int_{-\infty}^{\infty}M_{l,m,n}(\beta)\exp\{i\omega'[t-(\tau_1+n\tau)$$
$$-(m+1)\tau_1-l(2\tau_1-\tau)]\}d\omega', \quad (12)$$

where $M_{l,m,n}(\beta)$ is an amplitude factor that includes products of Bessel functions of orders l, m, and n. It follows from (12) that after the third pulse there appear signals at the instants of time $\tau_1+n\tau$, $(m+1)\tau_1$ and $l(2\tau_1-\tau)$, where $l, m, n=0, 1, 2, 3, \ldots$. It can also be shown that the terms discarded in accord with the condition $\beta^2 \ll 1$ yield responses at instants that are multiples of $2\tau_1-2\tau$ and $2\tau_1+\tau$.

D. Stimulated echo

If the third pulse is applied at an instant $\tau_1 \gg \tau_2$, then it is clear from physical considerations, and also mathematically on account of the factor $\exp(-\tau_2/T_2)$, that the system oscillations produced by the first two pulses prior to this instant have already attenuated. Consequently, the memory of the system can be related only to the residual changes of the natural frequency of the oscillators.

Earlier, when we examined processes that occur during relatively short time intervals, the change of the particle oscillation frequency under the influence of the pulses was regarded as irreversible. In the general case, however, we can assume the presence of a relaxation that returns the frequency to its initial value, with a certain time constant T_1, and it must therefore be taken into account if τ_1 are comparable with T_1. Thus, the value of the frequency of the particle after the third pulse is

$$\omega'''=\omega'+b\mathscr{E}_{1,2}\exp\left(-\frac{t-\tau}{T_1}\right)+b\Delta\mathscr{E}\exp\left(-\frac{t-\tau_1}{T_1}\right), \quad (13)$$

where $\Delta\mathscr{E}=\mathscr{E}_{1,2,3}-\mathscr{E}_{1,2}\exp[-2(\tau_1-\tau)/T_2]$ is the change of the energy of the particle oscillations after the third pulse, $\mathscr{E}_{1,2,3}$ is in analogy with (5) the square of the vector sum of the amplitudes of the oscillations after three pulses; $W'''=\exp(-a\Delta\mathscr{E}\Delta t_3)$.

Under these conditions, the sample polarization takes the form

$$P(t)=\frac{1}{2}\int_{-\infty}^{\infty}A_3\exp\left(-\frac{t-\tau_1}{T_2}\right)\exp[i\omega'''(t-\tau_1)]W''W'''G(\omega')d\omega'$$
$$=\frac{1}{2}\int_{-\infty}^{\infty}A_3\exp\left(-\frac{t-\tau_1}{T_2}\right)\exp[iO(\beta)-O(\alpha)]$$
$$\times\sum_{n=-\infty}^{\infty}(-i)^n J_n(\beta'+i\alpha)\exp(in\varphi_2)\exp[i\omega'(t-\tau_1-n\tau)]G(\omega')d\omega', \quad (14)$$

where

$$\beta'=2A_1A_2\exp(-\tau/T_2)\exp[-(t-\tau)/T_1]b(t-\tau_1).$$

In analogy with the case of a two-pulse echo, expression (14) describes at $n=0$ the response immediately after the third pulse, and at $n=1, 2, \ldots$ it describes respectively the first, second, etc., stimulated signals that appear at the instants $\tau_1+n\tau$. In the small-amplitude approximation ($\beta^2 \ll 1$, $\alpha=0$) we have for the first stimulated echo

$$P_1(\tau_1+\tau)\approx\frac{Ne^2}{2\sigma c}\gamma\omega_0 T_2 E_1 E_2 E_3\left[1-\exp\left(-\frac{\Delta t_1}{T_2}\right)\right]\left[1-\exp\left(-\frac{\Delta t_2}{T_2}\right)\right]$$
$$\times\left[1-\exp\left(-\frac{\Delta t_3}{T_2}\right)\right]b_E\tau\exp\left(-\frac{2\tau}{T_2}\right)$$
$$\times\exp\left(-\frac{\tau_1}{T_1}\right)\exp\left[i\left(\varphi_2-\frac{\pi}{2}\right)\right]g(t,\Delta t). \quad (15)$$

Calculation of the integral yields the shape of the echo signal:

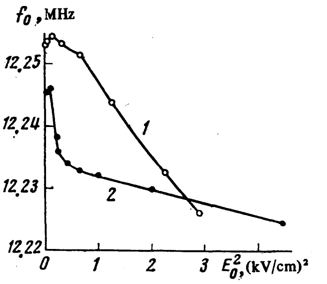

FIG. 1. Change of natural frequency of two individual particles as a function of the amplitude pulse ($KBrO_3$, $d \approx 135$ μm, $t = 20 = 20$ °C, $\Delta t = 20$ μ sec). The obtained values of b_E at $E_2^0 \geq 0.6$ $(kV/cm)^2$ are: curves 1—10.8 and 2—2.2 kHz $(kV/cm)^{-2}$.

$$g(t,\Delta t)=\frac{8}{\Delta t_1\,\Delta t_2\,\Delta t_3}\int_{-\infty}^{\infty}\frac{\sin(\omega'\Delta t_1/2)\sin(\omega'\Delta t_2/2)\sin(\omega'\Delta t_3/2)}{\omega'^3}\times\exp[i\omega'(t-\tau_1-\tau)]\,d\omega'. \tag{16}$$

E. Magnitude of signal

The foregoing analysis was carried out in terms of a polarization equal to the surface density of the electric charges and produced as a result of the inverse and direct piezoelectric effects when an electric-field pulse E_0 of duration Δt was applied:

$$P \approx \frac{\gamma e^2}{2c} E_0 \frac{N}{\sigma \Delta t}.$$

A sample polarized by two pulses and placed in a parallel-plate capacitor with capacitance C, will induce an echo-signal voltage $U_e = Psb_E E_0^2 \tau / C$, where $s \approx d^2$ is the area of the charged surface of the particle. The relative magnitude of the signal is

$$\frac{U_e}{U_s}=\frac{E_e}{E_0}=\frac{2\pi\gamma}{S_C}\frac{e^2}{\varepsilon c}\frac{S}{\sigma\Delta t}b_E E_0^2\tau,\quad S=Nd^2=\frac{P_0}{\rho d}, \tag{17}$$

where S_C is the area of the capacitor plates, ε is the dielectric constant (ε of the powder is less than ε_0 of the material), S is the total surface area of the particles, P_0 is the weight of the sample, ρ is the density of the material, and d is the dimension of the particles.

3. RESULTS OF EXPERIMENT

The literature abounds in experimental data, which will be discussed below in connection with the experimental data. We present here results of some additional measurements at a frequency 12.5 MHz, carried out on the apparatus briefly described in[14,15].

1. Of obvious interest is a direct study of the transient responses from the individual particles of the powder. To observe these responses from strong piezoelectrics it is necessary to make only two improvements in the standard technique: use a receiver with higher sensitivity (5–10 μV) and use a pickup capacitor with a small gap between the plates, $\delta = 0.33$ mm. When a single powder particle was excited in such a pickup, exponentially damped oscillations with piezoresonance frequency f_0, initial amplitude A_0, and damping time constant approximately equal to that obtained from the falloff of the two-pulse echo signal are observed after the termination of an exciting electric-field pulse ($\Delta t = 5$–20 μsec). As the natural frequency f_0 we fixed the central frequency of the RF pulse, corresponding to the maximum (resonant) amplitude A_0. This measurement is easy to perform in coherent apparatus. The singularities of the responses from individual piezoelectric particles with dimensions 100–200 μm are reported below.

a) The natural frequencies f_0 of particles sifted out to have a single dimension $d \pm 10\%$, differ noticeably from one another, and the observed number of resonant modes of one particle in the chosen frequency band 12.5 ± 1 MHz ranged from zero to six.

b) Most particles are characterized by a nonlinear dependence of the natural frequency f_0 on the intensity of the exciting pulse, similar to that shown in Fig. 1.

c) The change of f_0, due to the exciting pulse, does not vanish instantaneously when the exciting pulse is removed, but is characterized by a certain time constant T_1 of its return to the initial value. Application of a second pulse with amplitude $E_2 < E_1$ at the instant $t \ll T_1$ does not cause an additional change of f_0.

d) The times T_1 of individual particles were subject to considerable differences (from fractions of a second to dozens of minutes and more). The fastest recovery occurred in particles that were not crushed and shown by a microscope to have the highest transparency.

e) At large pulse amplitudes (3–5 kV/cm), a jump-like shift of f_0 outside the limits of the exciting-pulse spectrum was sometimes observed and amounted to hundreds of kHz.

2. We investigated the influence of cold working of the sample particles on the relaxation characteristics of the echo signals (KDP sample, $t = 22$ °C). From one package of the powdered KDP reagent we ground and sifted three equal batches ($d = 135 \pm 15$ μm, $P_0 = 1.3$ g) that differed in the cold working of the particles. Sample 1 was prepared by sifting from the fine-grain reagent without prior grinding. The force applied to the particles in the course of grinding was larger in the case of sample 3 than in the case of sample 2. Examination under an optical microscope has shown that the particles in samples 1, 2, and 3 had different transparencies: the most transparent were those of sample 1, and the least transparent in sample 3. The measurement results are listed below:

Sample No.	1	2	3
T_2, μsec :	185	130	175
T_1, sec:	0.3	$2\cdot10^3$	10

3. We plotted the echo-signal amplitudes as functions of the intensities (Figs. 2 and 3) and durations (Fig. 4) of the pulses in a wide range of their variation.

4. Figure 5 shows plots of the amplitudes of the echo signals as functions of the phase shifts between the first and second pulses φ_2. In the measurements, the phase of the reference voltage of the synchronous detector was set such that $A_{1e} = 0$ at $\varphi_2 = 0$.

5. Sample – $KBrO_3$ powder, passed through a sieve of mesh 135 ± 15 μm, sample weight 13.5 g, $t = 22$ °C,

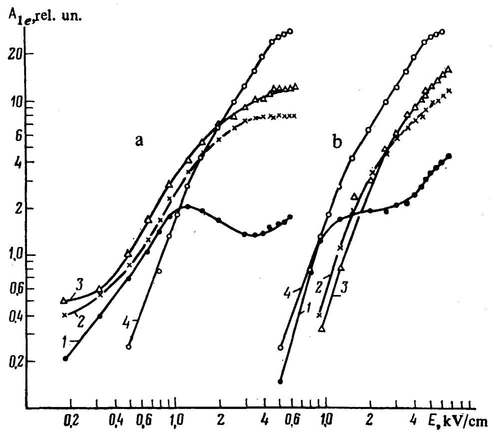

FIG. 2. Dependence of two-pulse echo of a Rochelle salt (RS) sample, with $d_{av} = 95$ μm, on the pulse amplitudes: a) curves: 1—$E_2 = 1.33$, 2—$E_2 = 3.3$, 3—$E_2 = 4.27$ kV/cm, 4—$E_1 = E_2$; b) curves: 1—$E_1 = 1.33$, 2—$E_1 = 3.2$, 3—$E_1 = 4.3$, 4—$E_1 = E_2$; $t = 0$ C, $\Delta t_{1,2} = 3$ μsec, $\tau = 20$ μsec.

pulse duration $\Delta t_{1,2,3} = 5$ μsec, pulse amplitude $E_{1,2,3} = 5$ kV/cm. Prior to the excitation of the sample by the pulse pairs, a single "reading" pulse was applied. If the powder particles were repeatedly stirred, the same monotonic decrease after the pulse was observed in all cases, thus showing the absence of any information connected with the prior history of the sample. The sample was next excited for 1 minute by pulse pairs with intervals $\tau = 25$ μsec and pair repetition frequency $F = 500$ Hz. An intense two-pulse echo signal was then observed. After the recording cycle, the sample was removed from the pickup, passed three times through a 200-μm sieve and placed in another pickup completely identical with the first. When only the single reading pulses were applied, the previously recorded stimulated-echo signal ($\tau = 25$ μsec) was observed, with a good echo/ring ratio (>10). The signal after the first sifted was seven times smaller than the initial signal (prior to sifter), but then remained unchanged after a second and third sifting.

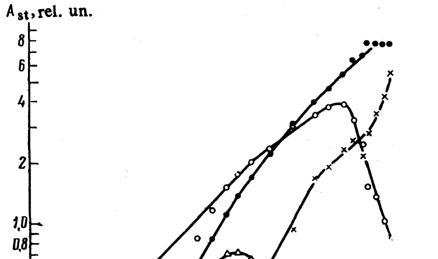

FIG. 3. Dependence of the magnitude of the stimulated echo of an RS sample, $d_{av} = 95$ μm, on the pulse amplitudes: 1—$E_{1,2} = 1.37$, 2—$E_{1,2} = 3.3$, 3—$E_{1,2} = 5.5$ kV/cm, 4—$E_1 = E_2 = E_3$; $t = 0$ C, $\Delta t_{1,2,3} = 4$ μsec, $\tau = 20$ μsec, $\tau_1 = 120$ μsec.

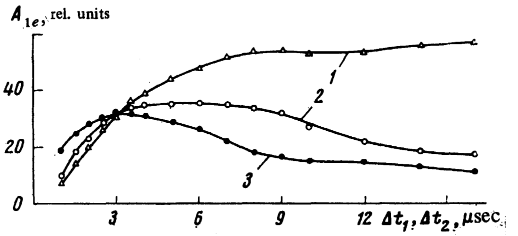

FIG. 4. Dependence of the two-pulse echo of KDP sample ($t = 77$ K, $T_2 = 100$ μsec, $d_{av} = 95$ μm, $f_0 = 20$ MHz, $\tau = 30$ μsec) on the pulse duration: 1—$\Delta t_1 = \Delta t_2$, 2—$\Delta t_1 = 3$ μsec, 3—$\Delta t_2 = 3$ μsec.

4. DISCUSSION AND COMPARISON WITH EXPERIMENT

1. The results given above (1b and 1e of Sec. 3) attest to the presence of nonlinearities of the form (3) and (4) and justify the use of Gould's oscillator model to describe the echo phenomenon. The values of the parameters b_E, determined from the curves of Fig. 1 for individual particles ($b_E = 10.8$ and 2.2 kHz(kV/cm)$^{-2}$) and from the ratio $A_{2e}(3\tau)/A_{1e}(2\tau) = 2b_E E_1 E_2 \tau \exp(-2\tau/T_2)$ obtained from (8) ($b_E \approx 11$ kHz(kV/cm)$^{-2}$) are in full agreement. The continuous spectrum of the values of T_1[11] is due to the scatter of the parameters b of the individual particles (see also Subsec. 1d).

2. In the explanation of the nature of the echo phenomenon itself and of its relaxation behavior, we assign an important role to the mechanism of the dislocation nonlinearity of the elastic properties. The prolonged recovery of the elastic modulus, which is typical of this mechanism (which consists of pinning of the dislocations by the point defects produced by the deformation) can be set in correspondence with the return of the natural frequency f_0 to the initial value after deformation by an external pulse (Subsecs. 1c and 1d, and (13)). To obtain agreement with the theory, the lifetime T_1 of the echo signal should be determined by the interaction of the sound with the dislocations. The measurements described above (Subsec. 2 of Sec. 3) were aimed at the study of this connection.

It is obvious that the sifted samples which were not crushed by us (KDP, $KBrO_3$), obtained by crystallization from the solution, have a lower dislocation density than the crushed samples. The increase of the dislocation density from sample 1 to sample 3 is confirmed by

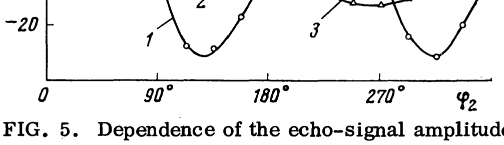

FIG. 5. Dependence of the echo-signal amplitudes on the phase shift φ_2 between the first and second pulse: 1—A_{1e}, 2—A_{2e}, 3—A_{st}.

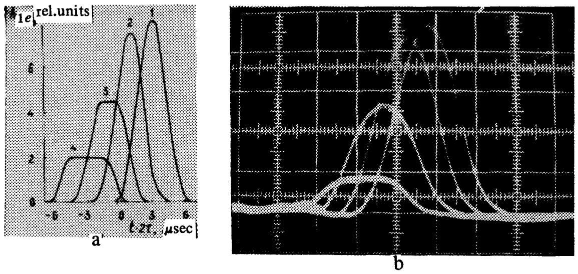

FIG. 6. Shape and shift of the maximum of a two-pulse echo: a) calculated curves—values of the integral (10); b) corresponding oscillograms $\Delta t_1 + 2\,\Delta t_2 = 7$ μsec, with the values of Δt_1 equal to 2.0, 3.0, 4.0, and 5.0 μsec for curves 1, 2, 3, and 4, respectively.

the different transparencies of samples 1, 2, and 3, since the presence of dislocations influences strongly the scattering of light in transparent crystals. [14] (We had no other means of directly estimating the dislocation density in crystals measuring 100–200 μm). We assume next that the time T_2 is of the order of the reciprocal of the sound damping coefficient in the sample particles. [14,17] It can therefore be stated that in sample 1, which has the lowest dislocation density, the damping of the sound is minimal, the intermediate dislocation density of sample 2 determines the maximum density, and the small difference between the values of T_2 of samples 1 and 3 can be attributed to the "rigid" grid of dislocations introduced into the crystal by the intensive cold working; the sound interacts weakly in this case with the dislocations. [18] The maximum value of T_1 in sample 2, with the maximal dislocation damping of the sound, may mean that it is precisely the interaction of the sound with the dislocation which produces the permanent echo picture.

3. The important role played by the piezoresonance condition is confirmed by the plots of $A_{1e} = f(d/\lambda_{ac})$, [14] the regular behavior of which begins at $d/\lambda_{ac} \geq \frac{1}{2}$. The same curves are completely described by the dependence (17) of the signal amplitude on S, N, P_0, and d. A numerical estimate of the signal for quartz ($P_0 = 1$ g, $d = 100$ μm, $\rho = 2$, $e = 5\times 10^4$ cgs esu/cm^2, $c = 8\times 10^{11}$ dyn/cm^2, $\sigma = 2$ (at $\varepsilon_0 = 4.5$), $S_C = 2$ cm^2, $\Delta t = 3$ μsec, $\sigma = 60$ MHz, [19,20] $b_E = 10$ kHz(kV/cm)$^{-2}$, $E_0 = 1$ kV/cm, $\tau = 30$ μsec) yields a value $E_e/E_0 \approx 4\times 10^{-4}$, which is of the same order as the experimentally observed value. Relation (17) can explain also the minima of the signal amplitude at the points of the phase transitions of the ferroelectrics, [14] where ε_0 is known to assume large values.

4. The factor $N/\sigma\Delta t$ in (9) and (15), taking relations (11) into account, determines the number of excited sample particles, inasmuch as N/σ is their spectral density, and $(\Delta t)^{-1}$ is the width of the spectrum of the frequencies of the exciting pulse, namely, a longer pulse having a narrower spectrum.

5. Expressions (8), (10), (12), and (16) describe the instant of appearance, the shape, and the widths of the observed different echo signals. [15,21,22] They are also illustrated in Fig. 6. Similar expressions for the echo at the instants 2τ and $\tau_1 + \tau$ were obtained in[5–7].

6. The values of the measured signals depend on a number of factors:

a) The dependences on the pulse amplitudes in the form $E_1E_2^2$, for the echo at the instant 2τ[22,23] and $E_1E_2E_3$ at the instant $(\tau_1+\tau)$[10] are given in[5–7]. However, as seen from (7), (9) and (14), (15) and from Figs. 2 and 3, this is valid only in the approximation of small pulse amplitudes. The subsequent nonlinear behavior at large amplitudes is described by Bessel functions, as described in Fig. 2 of[13].

b) The dependences of the signals on the durations of the pulses in the approximation of small amplitudes (9), (10) and (15), (16) agree well with the experimental data (Fig. 4) for short pulse durations.

c) The dependence of the signal on the phase shift φ_2 between the first and second pulses is given by formulas (8), (9), and (15) and is shown in Fig. 5.

d) The dependence of the signal on the frequency of the exciting field is linear in explicit form—see (9) and (15). However, a more complicated relation appears if the relation $T_2 = f(\omega_0)$ is specified. Thus, if we assume[17] $T_2 \sim \omega_0^{-1}$, then A_{1e} and A_{st} are proportional to ω_0^k, where $0 \leq k \leq 3$ depending on the value of $\Delta t/T_2$. In addition, it is natural to expect a frequency dependence of the quantity b.

7. The dependence of the signal on τ, as seen from (9) is not simply exponential, but as a factor τ. (This factor was obtained also in[5], but remained unobserved because of the absence of a damped exponential.) Therefore the function $\ln A_{1e}(2\tau) = f(\tau)$ constructed in the usual manner deviates from linearity at small values of τ. [14] The true value of T_2 should be determined from the straight line

$$\ln[A_{1e}(2\tau)/\tau] = \ln A_{1e}(0) - 2\tau/T_2.$$

For the echo at the instant $(n+1)\tau$ we obtain from (8) $A_{ne} \sim \exp(-2n\tau/T_2)$, i.e., it appears that T_2 is decreased by a factor n. Thus, for $A_{2e}(n=2)$ we have a decrease by a factor of two, as was in fact observed in[24].

5. CONCLUSION

1. On the basis of the Gould oscillator model, we developed a detailed theory of the echo phenomenon in piezoelectric powders, in which the deviation and the slow recovery of the piezoresonant mode of the particle after deformation by the ultrasound pulses is treated as a nonlinearity. The obtained solution agrees with all the known experimental results.

2. Experimental data were reported on the role of the interaction of sound with dislocations in polarization echo; these data show that the echo relaxation parameter T_2 reflects the dislocation losses, while T_1 characterizes the restoration of the elastic-modulus defect induced by the sound.

3. Recognizing that the interaction of sound with dis-

location occurs over a very large frequency spectrum, it can be assumed that the oscillator model and the theory developed here are applicable to cases of polarization echo is the decimeter and microwave bands, where the dislocation itself acts as a nonlinear oscillator.

4. The developed dislocation model and the form of the nonlinearity, on which the theory of the echo phenomenon in piezoelectric is based, can be used in principle also for other related echo phenomena.

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