Anomalous relaxation of polarization echo in piezoelectric crystals

V. M. Berezov, Ya. Ya. Asadullin, V. D. Korepanov, and V. S. Romanov

Kazan' Physico-technical Institute, USSR Academy of Sciences
(Submitted January 30, 1975; resubmitted June 18, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1674–1682 (November 1975)

Anomalously long times T_1 (on the order of a week or more) of stimulated echo (SE) signals of an electrical nature are observed in a number of piezoelectric crystals. The results of experiments with Rochelle salt samples are reported. The dependences of the SE on the temperature, biasing electric field, humidity of the medium and duration and intensity of the exciting pulses are investigated. An SE amplification effect is observed. The experimental results are discussed on the basis of a model of the polarization induced in the sample by alternating-field pulses. The induced polarization is due to the displacement of the charges (ions, defects, vacancies, etc.) in the piezoelectric field of the oscillations of the sample (powder particles), and "remembers" the spatial and time phase of these oscillations. The time T_1 is the induced-polarization lifetime.

PACS numbers: 77.30.+d

1. INTRODUCTION

A number of papers have been published in recent years on the observation and investigation of echo phenomena of an electrical nature in piezoelectric crystals (a rather complete bibliography can be found in ref. 1). One of the most important results of these researches is the observation of anomalously long relaxation times T_1 of the stimulated echo (SE), of the order of days or even months.[1] However, an echo with such properties has been observed only by illuminating photosensitive samples before or during the time of action of exciting pulses of an alternating electric field, and only at low temperatures.

We have obtained intense echo signals with T_1 on the order of a weak and more at room temperature, without any preliminary illumination of the sample. Responses of both the usual two-pulse echo and the stimulated echo were obtained only when the sample was ground into a powder, and the amplitude of the signal was maximal when the particle dimensions l satisfy the piezoresonance condition. Anomalously large values of the times T_1 were observed by us in the ferroelectric crystals KDP, ADP, Rochelle salt, $LiNbO_3$, and also in $KBrO_3$, NH_4Cl, $Bi_{12}GeO_{20}$, $Bi_{12}SiO_{20}$, sugar, tourmaline, quartz, and so on, which do not have ferroelectric properties, but which are piezoelectric. Results are given below of experimental studies of SE in Rochelle salt, which has interesting electric and electromechanical properties. The results are qualitatively explained on the basis of a model of piezoelectrically induced polarization.

2. METHOD OF EXPERIMENT

For the observation of the echo signals from piezoelectric samples and the measurement of their characteristics we used a coherent NMR relaxometer; the samples were placed not in an inductance coil but in a special pickup—the capacitor of a tank circuit. Application of a dc voltage to this capacitor allowed us to study the dependence of the echo signals on the electric field. For a study of the relaxation times, the sample was excited by a series of two or three pulses or a series of pairs of pulses and an additional probing pulse—in the case of the study of the effect of accumulation of the SE (see below).

The basic characteristics of the measurement setup are as follows: the amplitude of the alternating electric field was U = 200–2000 V/cm; tuning frequency $\omega/2\pi$ = 12.5 and 25 MHz; pulse length Δt = 1–10 μsec; dc electric field range E_0 = 100 to 15,000 V/cm; temperature range T = −196 to +200°C. The samples were prepared by grinding in a porcelain mortar and sifting through calibrated sieves. To observe the behavior of the echo signal as a function of the humidity the samples were placed in a special pickup with an open sample chamber.

3. RESULTS OF THE EXPERIMENT

It was noted above that the echo signals occur without any illumination of the sample. In particular, storage of the samples for several months in darkness or, conversely, irradiation of the sample by light of low intensity, did not affect the response appreciably. At the same time, the results of the experiments were very sensitive to such parameters as the temperature, the humidity, the dimensions of the particles, and even their mutual orientation in the pickup unit, and so on.

We studied the dependences of the SE amplitude and of the time T_1 in Rochelle salt on the temperature constant electric field, duration and power of the RF pulses, and also on the humidity of the medium. The experimental results can be formulated in the following fashion:

1) The amplitudes of the two-pulse echo and the SE grow monotonically with increase in the duration Δt_i and the power $\mathscr{P}_i$ of the exciting pulses. Unlike in spin echo, there is no periodic dependence here on Δt_i and $\mathscr{P}_i$. Saturation and a change in the shape of the response signals are observed upon further increase in the indicated parameters. Under optimal conditions, the SE intensity reached 0.1% of the power of the exciting pulses.

2. The following SE amplification takes place over the entire temperature range: if, instead of a single pair of excitation pulses, a series of N pairs is applied, followed by a single (probing) pulse (3-pulse), the amplitude of the SE turns out to be several times greater than for a single pair (Fig. 1). The amount of amplification depends on the repetition frequency f_N of the pairs

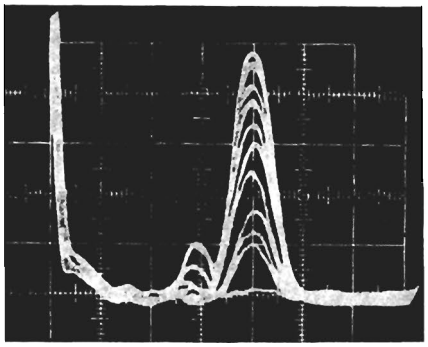

FIG. 1. Multiple exposure of SE signal for a change in the number of exciting pulse pairs from N = 3 to N = 2 × 10⁴; T = 20°C, l_{av} = 95 μ. ω/2π = 12.5 MHz, $\Delta t_{1,2,3}$ = 3 μsec, τ = 20 μsec, f_N = 250 Hz.

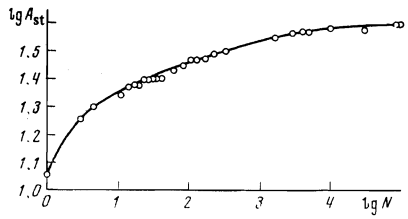

FIG. 2. Dependence of the SE amplitude (in relative units) on the number N of exciting pulse pairs.

and on the number of pairs N (Fig. 2). For a sufficiently large number of pairs, the signal reaches saturation. A similar effect was observed in the photosensitive CdS in ref. 1. We also note that application of a probing pulse after a single pair or a series of pairs does not erase of the phase memory. Furthermore, the SE signal is increased somewhat by multiple, even irregular, repetition of the 3-pulse.

Let the interval between the pulses of the pair be τ and let the interval between the pairs be greater than τ. The signals which arise within a time τ after the second pulse of each pair (the 2-pulse) are (except for the first signal) the sum of the double echo and the SE. The latter is excited by all the previous pairs and by the 2-pulse of the latter pair acting as a probing pulse.

Since the SE signal obtained after a series of pairs is more intense, and the results of measurements are less subject to random errors, we investigated in the main the responses excited by a series of pairs.

3) The amplitude of the two-pulse echo falls off in time like $\exp(-2\tau/T_2)$; the relaxation time T_2 changes from 25 μsec at the temperature T = 32°C to 120 μsec at T = −138°C. The temperature dependence of the time T_2 has maxima at the phase transition points. At the same time, it is known[2] that the relaxation times of acoustical oscillations have minima (the ultrasonic damping increases) near these points.

4) The experiments show that the exponential dependence of the SE amplitude on τ and τ_1 (τ_1 is the interval between the 1- and 3-pulses) of the form

$$A_{c\tau}=A_0 \exp(-2\tau/T_2-\tau_1/T_1) \quad (1)$$

is not satisfied relative to τ_1. In analogy with the result of Shiren et al.[3], the nonexponential decay indicates the presence of a distribution of the values of T_1. At the temperature T = 0°C, the values of T_1 range from $T_{1\,short}$ of the order of fraction of a second to $T_{1\,long}$

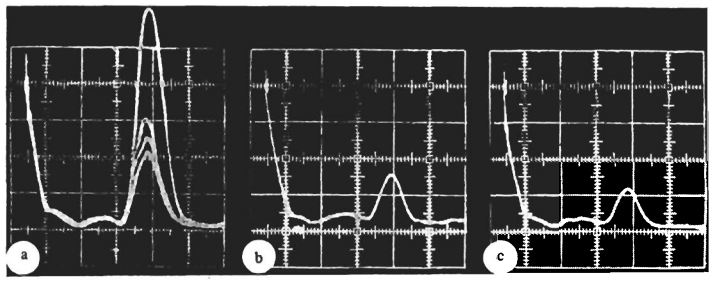

FIG. 3. Falloff of the SE amplitude with time. a) Reading downward: τ_1 = 0.001, 1, 10, 100 sec; b) τ_1 = 1 hr; c) τ_1 = 5 days. The gain of the receiver for all the oscillograms is the same. f_N = 500 Hz, N = 1.5 × 10⁴. The remaining parameters are shown in the caption of Fig. 1.

of the order of a week and more; the characteristic dependence of the SE amplitude on the time is shown in Fig. 3. With decrease in temperature, $T_{1\,long}$ increases and the amplitude of the usual echo and the SE fall off.

5) The application of a constant field E_0 in the ferroelectric region significantly shortens both $T_{1\,short}$ and $T_{1\,long}$ (Fig. 4), and in the paraelectric region, the dependence of T_1 on E_0 is very weak. (In nonferroelectric materials, in particular, in $Bi_{12}GeO_{20}$, the dependence of T_1 on E_0 also turns out to be weak.) At the same time, the application of E_0 during the action of the exciting pulses amplifies the signal: for $E_0 \approx 10$ kV/cm the SE amplitude increases by a factor of about 30 in the ordered phase and by 2- in the paraphase.

6) In addition to the dependence of the SE amplitude on the power of the pulses, already mentioned in Sec. 1, the times T_1 also depend on it. As is seen from Fig. 5, T_1 increases in proportion to the pulse-field amplitude. It is natural that the SE amplitude increases in proportion to the amount of sample investigated; it is interesting to note that T_1 increases at the same time.

7) In the lower paraelectric region, in addition to the sharp decrease in the SE amplitude at small τ_1 (of the order of fractions of seconds) and the slow decrease at large τ_1 (days, weeks), an exponential growth of the signal is observed in the intermediate region ($\tau_1 \sim$ 1—10 min, Fig. 6).

8) The SE amplitude depends strongly on the temperature stability during the time of measurement. Let the echo be excited at some temperature and within a time $t \gg T_{1\,short}$ and let the signal amplitude be equal to A_{st}. If we change the temperature by ±3—5 deg, the signal falls to one half its value. This process is reversible; upon a return to the temperature of excitation, the initial amplitude of the echo is almost completely regained without the application of new pairs of exciting pulses. The effect is not due to temperature gradients and depends only on the value of its shift.

9) Signals of both the ordinary echo and the SE are very sensitive to the humidity of the medium (air). When the humidity is increased in a small range, the signals fall off rapidly to the vanishing point. This process is also reversible to some extent relative to the SE; if, after passage of the exciting pulses, the humidity of the medium is increased, the amplitude of the response decreases; if the inverse process of drying out the medium follows, the response increases. However, this recovery is only partial, and takes place only for small changes in the humidity.

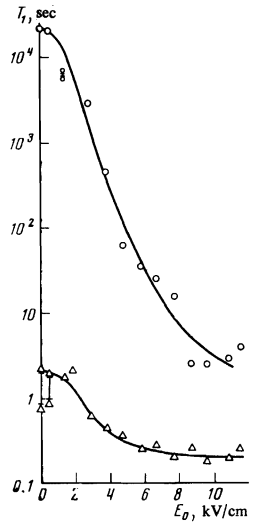

FIG. 4

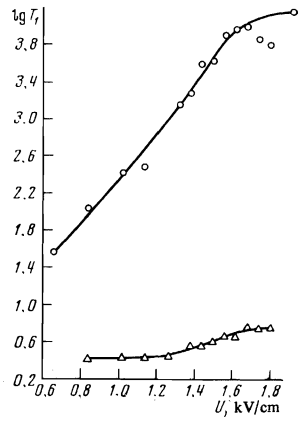

FIG. 5

FIG. 4. Dependence of the relaxation time T_1 on the constant electric field: Δ–T_1 short, ○–T_1 long. The value of T_1 short was estimated for τ_1 of the order of fractions of a second. In the estimate of T_1 long, the time τ_1 did not exceed 45 min; therefore, the shown values are undervalued relative to maximally long T_1. The temperature T = 0°C, l_{av} = 95 μ, $\omega/2\pi$ = 12.5 MHz, $\Delta t_{1,2,3}$ = 3 μsec, τ = 20 μsec, f_N = 500 Hz, N = 1.5 × 10^4.

FIG. 5. Dependence of the time T_1 on the pulse field amplitude; Δ–T_1 short, ○–T_1 long. All three pulses have the same amplitude. The other parameters are those of Fig. 4.

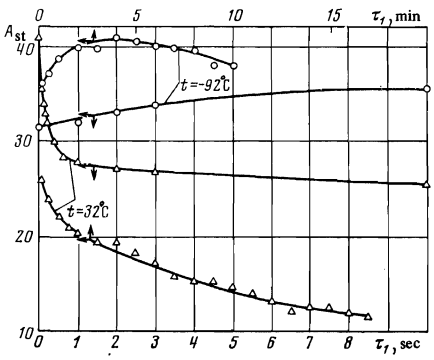

FIG. 6. Amplitude of the SE as a function of τ_1 for different temperature regions. The experimental conditions are those given in Fig. 4.

4. DISCUSSION OF THE EXPERIMENTS

It is quite evident that it is impossible to explain these results if we attribute the effect only to the acoustical properties of the system (i.e., to the piezoresonance oscillations of the powder particles. Evidently, the excitation of both the ordinary and the stimulated echoes is connected with the redistribution of charges (electrons in traps, ions or defects) in each of the particles of the powder. We now consider the interaction of the alternating-field pulses with the sample in somewhat more detail.

The 1-pulse field excites in the particle piezoresonant oscillations that constitute standing waves. Depending on the boundary conditions, one-half or one-quarter of a wavelength is spanned by the particle if the fundamental frequency of the oscillations is excited (Fig. 7). It is not necessary to speak more specifically about the type of oscillations, since the directions of the crystallographic axes of the particles are entirely random relative to the external field.

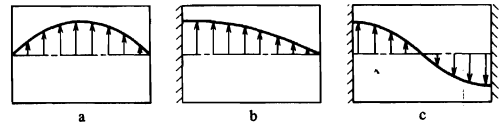

FIG. 7. Distribution of the deformations and the piezoelectric field in the case of oscillations of a beam: a) both ends free, b) one end clamped, c) both ends clamped. The arrows indicate the polarization amplitude.

The deformation wave induces in the material a piezoelectric field that oscillates in phase or out of phase with the deformation, depending on the sign of the piezoelectric constant. This field causes displacement or tunneling of the charges, which can be various vacancies, defects, or hydrogen ions. Excitation of electrons captured at shallow donor levels is also possible. An electric polarization P_i results. It is clear that this polarization is maximal at the antinode of the piezoelectric field, and falls off toward the node of the field. As a result of the action of the pulse, a spatially periodic coherent dipole moment of the polarization is induced both in the particle and throughout the entire macroscopic sample. We have in mind here the polarization produced both in the ordered and in the disordered phases. In the ferroelectric phase, moreover, the induced polarization acquires an additional contribution (see below).

After the passage of the pulse field, the phase of the polarization, which is coherent throughout the volume, rapidly disappears because of the reversible and irreversible relaxations; the reason for the reversible relaxation can be a) the difference between the frequencies of the natural oscillations of the sample particles, and b) the nonuniformity of the local electric field in the particle. Naturally satisfaction of the condition $T_2^* < T_2$ is necessary for observation of the echo, i.e., the reversible dephasing should occur more rapidly than the irreversible one. Thus, the phases of the microdipoles making up the periodic polarization in the particle (and in the entire sample) become completely incoherent within a time τ, with $T_2^* < \tau < T_2$. It should be emphasized that the polarization that is periodic in the particle (and in the sample) does not vanish here. Its lifetime is determined by the lifetime of the redistributed charges.

The formation of an echo at the time $t = 2\tau$ calls for nonlinearity of the interaction of the 2-pulse with the system, capable of reversing the evolution of the polarization phase in time. In the case of dielectrics, this nonlinearity can be due to the electrostriction term

$$H_2 = {}^1/_2 \eta \varepsilon E^2 S \qquad (2)$$

in the equation for the free energy. Here η is the electrostriction constant, ϵ the dielectric constant, E the external electric field, and S the deformation. For this mechanism, the nonlinear process of echo formation takes place only during the time of action of the pulse. Furthermore, continuation of the nonlinear process of echo formation after passage of the 2-pulse is possible, due to the piezoelectric and dielectric nonlinearities of the system.

The SE signal arises if a 3-pulse acts on the system at a time $\tau_1 > \tau$. In spite of the difference between the properties of the two-pulse echo and the SE, the latter is due to the nonlinearities of the interaction of the same type as the former.

As is seen from Eq. (1), in the interval $\tau_1 - \tau$, irreversible relaxation of the polarization phase has no effect on the amplitude of the response. The signal damping for fixed τ is determined by the "energy" relaxation, i.e., in our case, by the disruption of the periodic polarization. The anomalously large values of T_1 show that the redistribution of charges by the alternating field can be quite stable. We note that disruption of the polarization in each particle is not necessary for the complete destruction of the signal; it is sufficient to change the mutual location of the particles (to shake up the sample).

On the basis of the model outlined above, we now consider the experimental results.

1) The echo amplitude is determined by the value of the polarization at the moment of echo formation. It follows from the considered model that the polarization (and the signal amplitude) should depend linearly on Δt_1 and U_1 and nonlinearly on $\Delta t_{2,3}$ and $U_{2,3}$ (U_i is the the amplitude of the pulse field). Further increase in the signal with increasing duration Δt_i is prevented by the internal fields that cancel the action of the external fields, and also by the irreversible relaxation.

2) If the phase relations between the pairs of pulses are identical, then the polarization induced by each succeeding pair is added to the previous polarization, thus leading to amplification of the SE.

3) The dependence of T_2 near the Curie points can be explained if we assume that T_2 is the polarization relaxation time. It is known[4] that the relaxation time of the order parameter increases near the phase transition points (in our case the parameter is the polarization). Our experimental results agree also with the assumption[2] made to explain the character of the damping of the ultrasonic oscillations, that slow polarization processes take place in Rochelle salt, with $T_2 \sim (10^{-4}-10^{-5})(T_C - T)$. A hypothesis that a slowly relaxing polarization exists (in another ferroelectric) was also expressed in ref. 5.

4) The quantity T_1 is determined by the activation energy of the charges that form the polarization. The presence of a distribution of T_1 for a given temperature indicates the existence of a corresponding activation-energy spectrum. Furthermore, the regions $T_{1\,short}$ and $T_{1\,long}$ can be due to polarizations of a different nature (for example, electronic and ionic).

5) In the ordered phase, the polarization can be represented in the form

$$P=P_s+P_i, \quad P_s=P_{s0}+P_s(t),$$

where P_S is the spontaneous polarization and $P_S(t)$ describes the oscillations of the domain walls. It is clear that both the linear interaction

$$H_1=dPS$$

and, in particular, the nonlinear term (2) increase in this case. The latter term can be written in the form

$$H_2=GP^2S.$$

Here d is the piezoelectric coefficient and G the electrostriction coefficient.

The amplification of the signal upon application of the field E_0 can be due to several factors: first, P_S and P_i increase (in particular, because of the tunneling of charges in the constant field); second, the particles in the capacitor become grouped into columns between the electrodes in the case of dc fields on the order of several kV/cm and more. In this case the polarization axis (the ferroelectric axis) of the particles can become ordered relative to the direction of the field E_0 is possible. As to the shortening of the time T_1 with the field in the ferroelectric, the following reasons can be given: disruption of the induced polarization because of tunneling of the charges and their uniform redistribution, electrostatic dipole-dipole interaction inside the particles, and redistribution of the particles in a constant field.

6) When the pulse field amplitude is increased, the probability that the charges which produce the polarization will surmount higher barriers increases. It is evident that the lifetime of the polarization is proportional here to this probability (and to the echo amplitude).

7) The dependence of the SE amplitude on the temperature shows that the induced polarization is reversible in temperature. However, the nature of this reversibility is not clear.

8) Upon increase in the humidity of the medium, the moisture covers the surface of the particles, and the ions of the humid medium (air) screen the charges that form the polarization. The incomplete recovery of the SE signal when the sample is dried can be explained by assuming that the polarization of the particle decreases because of the recombination of the charges of the medium and of the particle or because of the surface conductivity.

Unfortunately, we have not succeeded in explaining the behavior of the SE shown in Fig. 6 (see Sec. 7 of the previous Section).

5. CONCLUDING REMARKS

We observed and studied the properties of the polarization echo which is easily observed in many piezoelectric dielectrics. It is shown that the relaxation times of the echo, T_2 and T_1, are the relaxation times of the phase and of the magnitude of the induced polarization. These times characterize the energy spectrum of the polarization charges (impurities, defects, and so on) and the interaction between them. Therefore the polarization echo can serve as a method of studying these inhomogeneities. Moreover, the large times T_2 and T_1 allow us to use these materials as memory cells.

[1] N. S. Shiren and E. L. Melcher, Proc. 1974 IEEE Ultrasonics Symposium, No. 11-14, 1974.
[2] G. G. Kessenikh, A. M. Shirkov, and L. A. Shuvalov, Kristallogr. **13**, 452 (1968) [Sov. Phys.-Crystallog. **13**, 367 (1968)].
[3] N. S. Shiren, R. L. Melcher, D. K. Garrod, and T. G. Kazyaka, Phys. Rev. Lett. **31**, 819 (1973).
[4] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).
[5] C. W. Fairall and W. Reese, Phys. Rev. **B8**, 3475 (1973).

Translated by R. T. Beyer
179