Properties of phonon electroacoustic echo in piezoelectric substances under resonance conditions

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The dependences of the parameters of two- and three-pulse phonon electroacoustic echoes are investigated experimentally and theoretically for various values of the parameters of the applied variable electric field pulses under acoustic resonance conditions. The dependence of the echo amplitude on the time interval between pulses was investigated. A sharp drop of both the two-pulse and three-pulse echoes was observed for radiofrequency pulses of long duration and high intensity. A theory has been developed which is an extension of the elementary perturbation method employed in an earlier work. The theory can explain the main properties of the experimentally observed echo signals.

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The present work is devoted to a detailed study of the properties of the electroacoustic echo in powders and accretions of crystals under conditions of acoustic resonance as a function of the regime of application of the radiofrequency pulses and of their parameters. The purpose of this research is the explanation of the features of the mechanisms responsible for the origin of the echo signals.

Electroacoustic echo of two types is observed experimentally, First, there is the two-pulse echo, discovered in Refs. 1 and 2. Its origin is connected with the nonlinear interaction of the acoustic oscillations in the grains of the powder or in individual crystals, excited by the first and second radiofrequency pulses.[3,4]

Large memory times of the stimulated echo at room temperature were discovered in Refs. 5 and 6, and independently in Refs. 7 and 8. According to Refs. 5 and 6, the relaxation time T_1 for the three-pulse phonon echo in crystalline powder of bismuth germanate exceeds several weeks at room temperature. According to Ref. 8, the relaxation time T_1 at 0 °C in Rochelle salt exceeds one week.

Such long relaxation times can be explained by the fixing in the powder grains of an electric-field component that is constant in time and nonuniform in space, and of strains that arise as a result of the nonlinear interaction of the acoustic oscillations excited by the first and second radiofrequency pulses. A record of this constant component contains information not only on the amplitudes, but also on the phases of the oscillations, and therefore, it is appropriate to call it an acoustic hologram. The third pulse of the field is the reading pulse, and the oscillations excited by it create the stimulated-echo signal.

In the theoretical description of the echo phenomenon, the powder was simulated by a system of nonlinear oscillators, the interaction between which could be neglected. For the description of the memory, we introduced some phenomenological parameters characterizing the departure of the crystal from the state of thermodynamic equilibrium. It was assumed that the lifetime of the nonequilibrium state significantly exceeds the damping time of the acoustic oscillations of the powder grains. The dependence of the signals of the two-pulse A_{2e} and three-pulse A_{3e} echoes on the amplitude and duration of the radiofrequency pulses is determined in lowest order perturbation theory by the expressions[3,9]

$$A_{2e} \sim E_{10} E_{20}^2 f_2(t-2\tau) \frac{1}{\Gamma} e^{-\Gamma\tau}(1-e^{-\Gamma\tau}), \tag{1}$$

$$A_{3e} \sim E_{10} E_{20} E_{30} f_3(t-T-\tau)\, \tau e^{-\Gamma\tau}, \tag{2}$$

where E_{10}, E_{20} and E_{30} are the amplitudes of the field in the first, second and third pulses; Δt_1, Δt_2, Δt_3 are the durations of the first, second and third pulses; τ and T are the intervals between the first and second and between the first and third pulses; Γ is the coefficient of sound attenuation.[1)] As is seen from (1) and (2), the dependence of A_{2e} and A_{3e} on τ has a nonmonotonic character. The functions $f_2(t)$ and $f_3(t)$ have the following characteristics:

a) $f_3(t)$ differs from zero in the range $|t| < (\Delta t_1 + \Delta t_2 + \Delta t_3)/2$;

b) if $\Delta t_2 = \Delta t_3$, then the maximum value of $f_3(t)$ amounts to $\frac{1}{4}\pi \Delta t_1(\Delta t_2 - \frac{1}{4}\Delta t_1)$ at $\Delta t_1 < 2\Delta t_2$ and $\frac{1}{4}\pi \Delta t_2$ at $\Delta t_1 > 2\Delta t_2$. In view of the symmetry of $f_3(t)$ relative to permutations of Δt_1, Δt_2, and Δt_3, similar formulas are obtained in the case of the same pulse duration of any of the pairs of pulses.

Since $f_3(t)$ degenerates into $f_2(t)$ at $\Delta t_2 = \Delta t_3$, the properties of $f_2(t)$ follow from the properties of $f_3(t)$.

The study was carried out with the NQR spectrometer IS-2. In view of the incoherence of the radiofrequency pulses used in the experiment, the amplitude A_{2e} of the two-pulse echo was measured by means of a storage oscilloscope with a single application of a pair of pulses, which simultaneously fulfilled the role of the pair recording an acoustic hologram in the sample. The amplitude A_{3e} of the three-pulse echo was measured by reading this hologram by the third pulse. Suppression of the two-pulse echo "2τ," formed by the recording pair was then observed, as revealed by a decrease in the amplitude and by a distortion of the shape of the echo in comparison with the two-pulse echo 2τ, observed following multiple input of pulse pairs. If the previous hologram in the sample is not erased, then the effect of suppression of the two-pulse echo is not

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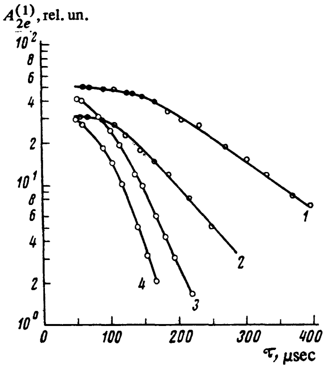

FIG. 1. Dependence of the amplitude of the two-pulse echo $A_{2e}^{(1)}$ on the time interval τ between pulses for $Bi_{12}GeO_{20}$ crystalline powder at room temperature: 1—$T_2 = 260$ μsec, $E_{10} = E_{20} = 2.2$ kV/cm, $\nu = 9$ MHz; 2—$T_2 = 150$ μsec, $E_{10} = E_{20} = 1.1$ kV/cm, $\nu = 9$ MHz; 3—$T_2 = 80$ μsec, $E_{10} = E_{20} = 2.2$ kV/cm, $\nu = 16$ MHz; 4—$T_2 = 65$ μsec, $E_{10} = E_{20} = 1.1$ kV/cm, $\nu = 16$ MHz.

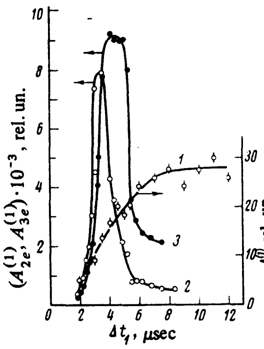

FIG. 3. Dependence of the amplitude of the two-pulse echo $A_{2e}^{(1)}$ (curves 1, 2) and the three-pulse echo $A_{3e}^{(1)}$ (curve 3) on the duration of the first pulse Δt_1 for $Bi_{12}GeO_{20}$ crystalline powder at room temperature, $\nu = 28$ MHz; 1—$\Delta t_2 = 3.5$ μsec, $E_{10} = E_{20} = 0.9$ kV/cm, 2—$\Delta t_2 = 5.2$ μsec, $E_{10} = E_{20} = 2$ kV/cm, 3—$\Delta t_2 = \Delta t_3 = 5.2$ μsec, $E_{10} = E_{20} = E_{30} = 3$ kV/cm.

observed. The stimulated echo obtained by reading the new resultant hologram has then a very small amplitude. The recording of the acoustic hologram by a succession of several (on the order of ten) pairs of noncoherent pulses is apparently ineffective because of the random nature of the phases of the radiofrequency pulses, which leads to an averaging of fields and strains produced by the separate pairs in the process of hologram recording. In the case of the application of coherent pairs of pulses, summation of the holograms is observed.[10]

The experimental results are shown in Figs. 1–4. The dependences of the amplitudes of the two-pulse and three-pulse echoes on the duration of the applied pulses for $Bi_{12}GeO_{20}$ powder were obtained in the single-pulse mode, while all three remaining were in the regime of multiple input of pairs.

Comparison of the experimental data[6,11] and of Figs. 1–4 with formulas (1)–(2) leads to the following results:

1. At not too long pulse lengths, in the range of fields studied, the theory describes well the dependence of the amplitude of the signal on the amplitude of the field of the pulses both for the two-pulse echo and the stimulated echo:

$$A_{2e} \sim E_{10}E_{20}^2, \quad A_{3e} \sim E_{10}E_{20}E_{30}.$$

2. The theory correctly describes the duration of the echo signal $\Delta t_e = \Delta t_1 + 2\Delta t_2$ for the two-pulse echo, and $\Delta t_e = \Delta t_1 + \Delta t_2 + \Delta t_3$ for the stimulated echo.

3. The theory correctly describes the dependence of the echo amplitude on the length of the interval between the first and second pulses in crystalline piezoelectric powder.

Figure 1 shows the dependence of A_{2e} of τ at different values of T_2. Different relaxation times T_2 were obtained for the same sample of $Bi_{12}GeO_{20}$ because of the dependence of T_2 on the frequency[12,13] and on the field intensity[14] of the applied pulses.[2)] The small flat areas of these curves confirm the prediction of the theory of Ref. 3, according to which A_{2e} should pass, with increase in τ, through a maximum whose location shifts in the direction of larger τ upon increase in T_2. Observation of A_{2e} at small τ is made difficult by the blocking of the detector after the radiofrequency pulse. Nevertheless, we shall assume that the existing data confirm the conclusion made in Ref. 3 that a predominant contribution is made to the echo formation by a purely acoustic nonlinearity of the type $c^{(3)}u^3$, where $c^{(3)}$ is the third-order elastic modulus.

4. At $\Delta t_2 = \Delta t_3 = \text{const}$, the theory indicates a growth in the amplitude of the stimulated echo and its subsequent saturation with increase in Δt_1. A similar con-

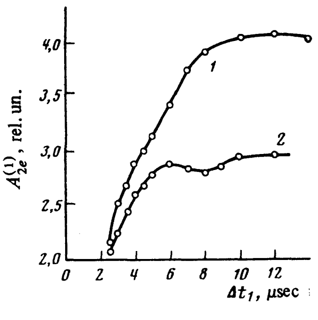

FIG. 2. Dependence of the amplitude of the two-pulse echo $A_{2e}^{(1)}$ on the duration of the first pulse, Δt_1, for an accretion of SbSI crystals at $T = 100$ °C, $\nu = 28$ MHz, $E_{10} = E_{20} = 3$ kV/cm; 1—$\Delta t_2 = 4$ μsec; 2—$\Delta t_2 = 2.2$ μsec.

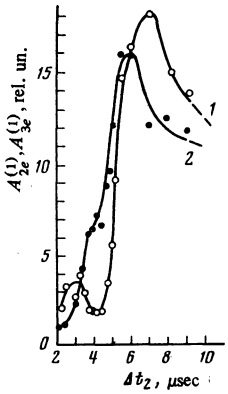

FIG. 4. Dependence of the amplitude of the two-pulse echo $A_{2e}^{(1)}$ (curve 2 and the three-pulse echo $A_{3e}^{(1)}$ (curve 1) on the duration of the second pulse Δt_2 at room temperature, $E_{10} = E_{20} = E_{30} = 3$ kV/cm, $\nu = 28$ MHz, $\Delta t_1 = \Delta t_3 = 4$ μsec.

clusion is obtained at $\Delta t_1 = \Delta t_3$ = const and with increase in Δt_2. In the case of a two-pulse echo, at Δt_2 = const and with increase in Δt_1, saturation of A_{2e} should occur at $\Delta t_2 = \Delta t_1/2$, while at Δt_1 = const and with increase in Δt_2 the amplitude of the echo should increase initially quadratically and then, at $\Delta t_2 = \Delta t_1/2$, according to a linear law. As is seen from Figs. 2 and 3 (curve 1), such a behavior of the amplitude of the echo is observed only at small external fields and short pulse lengths, which do not lead to large amplitudes of the oscillations. The eventual saturation of the $A^0_{2e} = f(\Delta t_1)|_{t_2=\text{const}}$ curves occurs at $\Delta t_1 \approx 2\Delta t_2$, in correspondence with the prediction of the theory. At large field amplitudes, in place of the expected saturation, a sharp decrease in the amplitude is observed of both the two- and the three-pulse echoes (see Figs. 3 and 4).

In addition, the curves in Fig. 4 also have weak singularities in the region $\Delta t_2 \approx \Delta t_1$: a relative maximum of the amplitude of the three-pulse echo and a minimum of the amplitude of the two-pulse echo. These singularities appear in the case of short pulse lengths up to the onset of the falloff (see Fig. 4). The durations at which the amplitude falloff begins depend on many factors. However, the larger the amplitude of the resonance oscillations of the particles, the earlier the falloff begins.

Thus, we may draw the conclusion that the existing theory is evidently limited by the condition that the amplitudes of the oscillations of the powder grains be small enough. In the framework of the model of a system of interacting nonlinear oscillators, the increase in amplitude leads to the result that the nonlinearity of each oscillation cannot be taken into account by means of elementary perturbation theory. It should be kept in mind that the nonlinear effects leads to a frequency shift that depends on the amplitude. A calculation of this type has already been carried out for the cyclotron echo.[15] Using equations formulated in Refs. 3 and 9, it is not difficult to carry out this calculation for the electroacoustic echo in powders. As a result, the two-pulse echo looks like a series of signals $A_{2e}^{(k)}$ that appear at the times $t=(k+1)\tau (k=1, 2, \ldots)$, the shape of which is described by the expression

$$A_{2e}^{(k)}(t) = -\sum_\lambda \frac{Q_\lambda p_\lambda}{2}\left[iE_1(\Omega_\lambda)J_{k+1}(b_{\lambda k}) + E_2(\Omega_\lambda)J_k(b_{\lambda k})\exp\left\{\frac{\Gamma_\lambda\tau}{2}\right\}\right] \times\exp\left\{-(k+1)\frac{\Gamma_\lambda\tau}{2} - k\left[i\psi_{\lambda 1}(\tau) - i\frac{\pi}{2}\right] + ia_{\lambda k} - i\Omega_\lambda t\right\}. \tag{3}$$

Here

$$a_{\lambda k} = \frac{s_\lambda Q_\lambda^2}{4\omega^2\Gamma_\lambda}[E_1(\Omega_\lambda)\exp\{-\Gamma_\lambda\tau\} + E_2^2(\Omega_\lambda)](1-\exp\{-\Gamma_\lambda k\tau\}), \tag{4}$$

$$b_{\lambda k} = \frac{s_\lambda Q_\lambda^2}{2\omega^2\Gamma_\lambda}E_1(\Omega_\lambda)E_2(\Omega_\lambda)\exp\left\{-\frac{\Gamma_\lambda\tau}{2}\right\}(1-\exp\{-\Gamma_\lambda k\tau\}), \tag{5}$$

$$\psi_{\lambda 1} = \frac{s_\lambda Q_\lambda^2}{4\omega_\lambda^2\Gamma_\lambda}E_1^2(\Omega_\lambda)(1-\exp\{-\Gamma_\lambda\tau\}), \tag{6}$$

$\Omega_\lambda = \omega - \omega_\lambda$ is the difference between the frequency of the external field ω and the natural frequency ω_λ of one oscillator; Γ_λ is the damping coefficient of the oscillator λ; Q_λ and p_λ are coefficients which characterize the piezoeffect of a single powder grain; s_λ is the coefficient characterizing the nonlinear shift in the natural frequency of the oscillator; $J_k(t)$ is a Bessel function, $\tilde{E}_j(\Omega)$ is the Fourier amplitude of the j-th pulse of the field:

$$E_j(\Omega) = \int_{-\infty}^{+\infty} E_j(t)e^{i\Omega t}dt \tag{7}$$

(for simplicity, it is assumed to be real). In the case of pulses of rectangular shape and of length Δt_j,

$$E_j(\Omega) = E_{j0}\frac{\sin(\Omega\Delta t_j/2)}{\Omega/2}. \tag{8}$$

Account of the nonlinearity for the stimulated echo can be carried out in similar fashion. After the second radiofrequency pulse there is in each powder grain a deformation that is constant in time, the amplitude of which is proportional to

$$\overline{C_\lambda^2} = \frac{Q_\lambda^2}{4\omega_\lambda^2}\left\{E_1^2(\Omega_\lambda)\exp\{-\Gamma_\lambda\tau\} + E_2^2(\Omega_\lambda) + 2E_1(\Omega_\lambda)E_2(\Omega_\lambda) \times\exp\left\{-\frac{\Gamma_\lambda\tau}{2}\right\}\cos[\omega_\lambda\tau - \psi_{\lambda 1}(\tau)]\right\}\exp\{-\Gamma_\lambda(t-\tau)\}, \tag{9}$$

and the electric field is proportional to this deformation. Without specifying the memory mechanism, we consider only the case of sufficiently small $\overline{C_\lambda^2}$. Then the equation for the parameter $\eta(\mathbf{x}, t)$, which describes the memory, can be written in the form[9]

$$\mu\partial\eta/\partial t = -\Lambda_\lambda(\mathbf{x})\overline{C_\lambda^2}, \tag{10}$$

where μ is a kinetic coefficient and $\Lambda_\lambda(x)$ is the coupling coefficient between the oscillator λ and the parameter η. The equation of oscillations of the oscillator λ is, in turn, of the form

$$\frac{d^2C_\lambda}{dt^2} + \Gamma_\lambda\frac{dC_\lambda}{dt} + \left[\omega_\lambda + \frac{1}{\rho}\int\Lambda_\lambda\eta d^3x\right]C_\lambda = 0. \tag{11}$$

In order to take into account the memorization of the state after the second radio-frequency pulse, we must substitute Eq. (9) in (10). Assuming $T \gg \Gamma^{-1}$, we can determine the value of η that is obtained as a result of the memorization, integrating (10) from $t=\tau$ to infinity. Substituting the resultant expression in (11), we can determine the character of the oscillations that arise after the third radiofrequency pulse. As a result, a series of signals $A_{3e}^{(k)}$ is obtained for the stimulated echo, at the times $T+k\tau (k=1, 2, 3, \ldots)$, the shape of which is determined by the expression

$$A_{3e}^{(k)} = -\sum_\lambda \frac{Q_\lambda p_\lambda}{2}E_3(\Omega_\lambda)i^kJ_k\left[k\frac{Q_\lambda^2R_\lambda\tau}{4\omega^3\Gamma_\lambda}E_1(\Omega_\lambda)E_2(\Omega_\lambda)\exp\left\{-\frac{\Gamma_\lambda\tau}{2}\right\}a_T\right] \times\exp\left[-\frac{\Gamma_\lambda}{2}k\tau - i\Omega_\lambda t + i\psi_{\lambda 3}(k\tau)\right], \tag{12}$$

where

$$\psi_{\lambda 3}(k\tau) = \frac{Q_\lambda^2 p_\lambda}{8\omega^3\Gamma_\lambda}k\tau[E_1^2(\Omega_\lambda) + E_2^2(\Omega_\lambda)]a_T + \frac{s_\lambda Q_\lambda^2}{4\omega^2\Gamma_\lambda}E_3^2(\Omega_\lambda)(1-\exp\{-\Gamma_\lambda k\tau\}), \tag{13}$$

$$R_\lambda = \frac{1}{\mu\rho V_\lambda^{5/3}}\int_{V_\lambda}\Lambda_\lambda d^3x, \tag{14}$$

V_λ is the volume of the grain, a_T is a factor that takes into account the relaxation of η in the time T (we assume that $\tau \ll T$, and that we can neglect the relaxation of η in the time τ).

The expressions thus obtained contain, in principle, all the information on the amplitude and shape of the pulse echoes. They allow us to conclude that $A_{3e}^{(k)}$ has the same dependence on E_{10}, Δt_1 and on E_{20}, Δt_2, since $\tilde{E}_1(\Omega)$ and $\tilde{E}_2(\Omega)$ enter into (12) in identical fashion. This conclusion agrees completely with the experimental data (curves 2 and 3 in Figs. 3 and 4).

For a more detailed investigation, we can carry out the averaging of (3) and (12) over all configurations of the grains and replace the summation over λ by integration over Ω with a certain natural-frequency density distribtuion $n(\omega+\Omega)$. Since the important part of the contribution to the current is made by an Ω interval of order $(\Delta t)^{-1}$, and $n(\omega)$ changes over a much greater interval W/r (W is the sound velocity and r the characteristic dimension of the grain), we can put $n(\omega+\Omega) = n(\omega)$. The possibility of averaging as applied to the existing experiments is not obvious. As experiment shows, the echo amplitude can change significantly, for example, after shaking the test tube with the powder. For this reason the parameters of the grains can be simply replaced by their average values with sufficient accuracy.

The integrals obtained are still rather complicated, and we limit ourselves to calculation of the asymptotic form at $\Delta t_1 \gg \Delta t_2$, Δt_3. Here we shall assume that the field amplitudes are not too great, so that weak-signal theory is applicable for pulses with duration of the order of $\Delta t_2 \sim \Delta t_3$. The asymptotic calculation of the integrals is carried out in the Appendix. As a result, we obtain

$$A_{3e}^{(k)} \sim (\Delta t_1)^{-2}, \quad A_{2e}^{(k)} \sim (\Delta t_1)^{-2}.$$

We now consider the physical reasons of such a behavior, for example, for A_{3e}. We recall that the radiofrequency pulse excites the acoustic oscillations only in those grains which are at resonance with it.

The change in $A_{3e}^{(k)}$ upon increase in Δt_1 is connected with two circumstances. First, the recorded signal increases, which leads to a change in the amplitude of the oscillations creating an echo readout. So long as the recording is weak, the amplitude of these oscillations is small and increases with amplification of the recording. This corresponds to the weak-signal theory, when the quantity $\psi_{\lambda 3}$ can be neglected and the Bessel function replaced by the first term in its series expansion. In the case of a sufficiently strong recording, the amplitude of these oscillations increases so much that a role is assumed by nonlinear effects (the same which led to the formation of a dc component in the recording). The nonlinear effects lead to a shift in the frequency of the oscillations, as a result of which the resonance between the recording and the reading pulses disappears and the amplitude of the oscillations that produce the echo ceases to increase. Second, the influence of the increase of Δt_1 on $A_{3e}^{(k)}$ is connected with the fact that the quantity Δt_1 determines the spectral width of the first pulse of the field. At $\Delta t_1 \gg \Delta t_2$, Δt_3, the spectrum of this pulse becomes so narrow that it determines the number of oscillators taking part in the recording process. With increase in Δt_1 the number of oscillators falls off, and the amplitude of the signal falls off correspondingly. In the calculation of the integral, the phase relations between the oscillations of the different oscillators is taken into account, as a result of which A_{3e} falls off more rapidly than $(\Delta t_1)^{-1}$. The behavior of A_{2e} can be explained in similar fashion.

Thus the qualitative character of the plots in Fig. 3 is described by the expressions (3) and (12). A better agreement (a maximum of $A_e(\Delta t_1)$ at $\Delta t_1 \approx \Delta t_2$) is obtained in the case of shorter durations and smaller amplitudes of the exciting pulses, in full agreement with the conditions that limit the applicability of the considered approximation.

In order to try to explain the suppression of the first series of signals of the two-pulse echo in samples where memory is well apparent, we need to take into account the effect of the memory on the two-pulse echo. This effect is manifest in the fact that the oscillations which appear after the second radiofrequency pulse not only take part in the recording, but also reproduce this recording.[9] For the calculation of the corresponding contribution we also need to make use of Eq. (13) in the description of the oscillations arising after the second pulse. As a result we must add the corresponding additional contributions to expressions (4) and (5) for $a_{\lambda k}$ and $b_{\lambda k}$:

$$a_{\lambda k}' = -\frac{R}{2\omega_\lambda \Gamma_\lambda}\left(\frac{Q}{2\omega_\lambda}\right)^2 \left[k\tau - \frac{1}{\Gamma_\lambda}(1-\exp\{-\Gamma_\lambda k\tau\})\right] \times [\tilde{E}_1^2(\Omega_\lambda)\exp\{-\Gamma_\lambda \tau\} + \tilde{E}_2^2(\Omega_\lambda)], \tag{15}$$

$$b_{\lambda k}' = -\frac{R}{\omega_\lambda \Gamma_\lambda}\left(\frac{Q}{2\omega_\lambda}\right)^2 \left[k\tau - \frac{1}{\Gamma_\lambda}(1-\exp\{-\Gamma_\lambda k\tau\})\right] \times \tilde{E}_1(\Omega_\lambda)\tilde{E}_2(\Omega_\lambda)\exp\left\{-\frac{\Gamma_\lambda \tau}{2}\right\}. \tag{16}$$

It is not difficult to note that the expressions (4), (5) and (15), (16) depend differently on the number of the signal k. It can be assumed that at small values of k, the coefficients $a_{\lambda k} + a'_{\lambda k}$ and $b_{\lambda k} + b'_{\lambda k}$ are small as a result of the partial mutual cancellation of the terms which leads to the suppression of the echo signals. At large values of k, the quantities $a'_{\lambda k}$ and $b'_{\lambda k}$ turn out to be larger than $a_{\lambda k}$ and $b_{\lambda k}$ respectively, and cancellation does not take place. However, it is necessary to take account of the fact that this explanation of the suppression of the first echo signal presupposes such values of the parameters determining the nonlinear effects and such a connection between the deformation and the parameter η, that the quantities $a_{\lambda k}$ and $a'_{\lambda k}$, and also $b_{\lambda k}$ and $b'_{\lambda k}$, turn out to be of the same order and their mutual cancellation is possible in principle. The present status of the experiments does not allow us to draw any final conclusions.

We note that in the calculation of the expressions (3) and (12), for simplicity, we have not taken into account the dependence of the damping coefficient Γ on the amplitude of the oscillations of the oscillator (on account of the higher harmonics). Moreover, the damping coefficient was assumed to be so small that $\Delta t_j \Gamma \ll 1$. Under the experimental conditions, the latter approximation is entirely valid.

Supplementing the calculation that has been carried out, we must make one remark. Equation (10) was written down under the assumption that the quantity η in a certain volume element of the crystal depends only on the state of this element. However, in practice, we can encounter another case, for example, when η has the meaning of the concentration of electrons or defects. In this case, η obeys the conservation law

$$\frac{\partial \eta}{\partial t} + \frac{\partial j_k^\eta}{\partial x_k} = 0, \quad j_k^\eta = -\sigma_{kl}^\eta \frac{\partial}{\partial x_l} \frac{\delta F}{\delta \eta}, \tag{17}$$

where F is the free energy per unit volume.

The expression for the flux density j_k^η is written with the help of the general principles of irreversible thermodynamics. At small departures from thermal equilibrium, the kinetic coefficient σ_{kl}^η can be assumed to be constant. It is not difficult to establish the fact that Eq. (17) deals in practice to the same results as Eq. (10). The difference lies only in the change in the frequency dependence, which is not studied in the present research, and in the fact that the coupling constant is different. The results also do not change if we take into account both the relaxation (10) and the transfer of η (17).

Thus the existing theory explains the basic experimental data. Within the framework of this theory, it is not difficult to explain other similar phenomena, such as the ringing observed after each radiofrequency pulse. In the simplest case it suffices for this purpose to set $n(\omega) = 0$ at $\omega < \omega_{\min} \sim W/r$ and $n(\omega) = \mathrm{const}$ at $\omega > \omega_{\min}$.[3)] We note that the action of the pulse on itself, i.e., "self-echo" of the pulse[16] can contribute to the ringing. When asserting that the existing theory agrees with experiment, we must note one more problem which does not have a unique answer at the present time. This is the problem of the mechanism of the memory. At the present time, there are two mechanisms discussed in the literature which can apparently occur in powders. The first of these is the redistribution of the electrons among the traps. Such a redistribution can take place either through ionization of the charged traps by a strong field, which can occur in CdS single crystals at helium temperatures,[17] or by thermal activation.[18,19] The second possible mechanism is the redistribution of point defects or dislocations.[5]

The difficulties that arise are connected with the fact that knowledge of the properties of the individual grains of the powder is necessary to explain the memory mechanism. These properties can differ significantly from the properties of the single crystal from which the powder is obtained. Actually, grinding the single crystal can produce both neutral dislocations and point defects capable of capturing electrons.

Recently, Chaban[20] and Melcher and Shiren[21] proposed another mechanism of memory in powders, connected with the rotation of the grains during the time of the second radiofrequency pulse. In the experiments described in the present work, this mechanism evidently makes no definite contribution for the following reasons. First, this mechanism explains the appearance only of a single echo signal at the instant of time $T + \tau$ and not of a series of signals at the times $T + k\tau$. Second, it is difficult to explain by this mechanism the experimentally observed simultaneous existence of two recordings produced in sequence, one after the other, and at the same frequency, but with different intervals τ_1 and τ_2 between the first and second radiofrequency pulses, and it is also difficult to explain the onset of combined echo signals "$T + (\tau_1 + \tau_2)$" and "$T + (\tau_1 - \tau_2)$."

Figure 5 represents three oscillograms of the echo signal, read out by one radiofrequency pulse from two individual recordings (a, b) and one combined recording (c). Finally, we must note that the formula (12) does

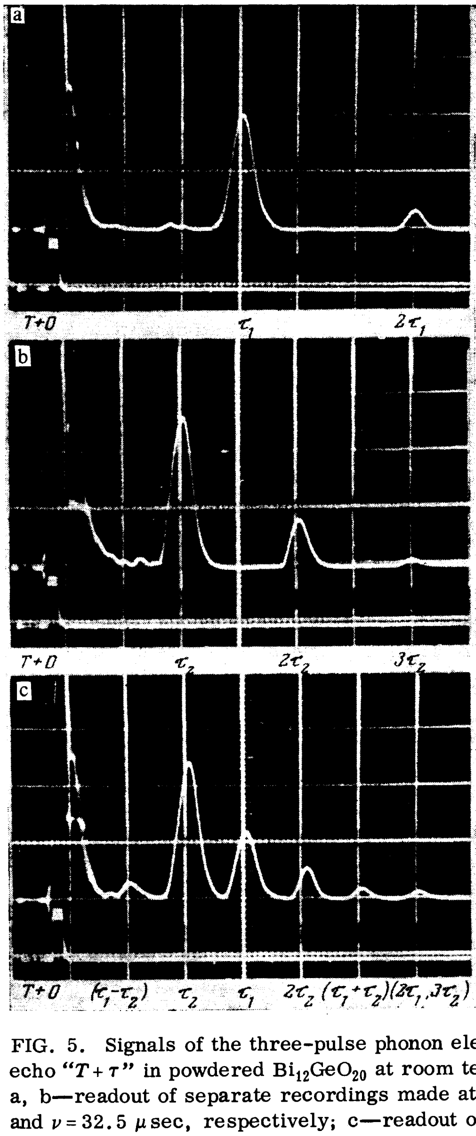

FIG. 5. Signals of the three-pulse phonon electro-acoustic echo "$T + \tau$" in powdered $Bi_{12}GeO_{20}$ at room temperature; a, b—readout of separate recordings made at $\nu = 24.7\ \mu$sec and $\nu = 32.5\ \mu$sec, respectively; c—readout of recording which appears as a result of the superposition of the second recording ($\tau = \tau_2$) on the first ($\tau = \tau_1$). The sweep of the oscilloscope was started by the third, i.e., reading, pulse at the instant of time $t = T$.

not apply to the orientation mechanism. In particular, with increase in Δt_1, this mechanism can evidently lead only to saturation of the signal $A_{3e}^{(1)}$, but not to its decrease with increase in Δt_2—only to an increase in the signal. Comparison of the mechanisms of memory is made difficult also by the fact that the quantitative theory of the orientation mechanism exists at the present time only for freely falling powder grains.

In conclusion, we thank A. A. Chaban for discussion of problems connected with the memory mechanism.

APPENDIX

1. An investigation of the integral obtained from (12) reduces to an investigation of the asymptotic form of the function

$$F_k(\lambda)=\int_0^\infty f_k\left(\lambda\frac{\sin x}{x}\right)dx,\quad f_k(z)=J_k(z)e^{iaz^2}$$

as $\lambda\to\infty$, $k>0$. It is convenient to rewrite the function $F_k(\lambda)$ in the form

$$F_k(\lambda)=\sum_{n=0}^{\infty}\int_{x_n}^{x_{n+1}} f_n\left(\lambda\frac{\sin x}{x}\right)dx,$$

where x_n is the non-negative root of the equation $\tan x=x$. At not too large n, when $\lambda\gg n\pi$, the immediate vicinities of the points $x=n\pi$ are significant in the integral. On the other hand, when $n\gg1$, we can set $x_n=n\pi+\pi/2$ and the change over the integration interval can be assumed to be small in comparison with $n\pi$. Recognizing that the parity of $f_k(z)$ is identical with the parity of k, we obtain the following approximate formula

$$F_k(\lambda)\cong[1+(-1)^k]\sum_{n=1}^{\infty}\int_0^{\pi/2} f_k\left(\frac{\lambda\sin y}{n\pi}\right)dy$$

$$-[1+(-1)^n]\lambda\frac{\partial}{\partial\lambda}\sum_{n=1}^{\infty}\frac{(-1)^n}{n\pi}\int_0^{\pi/2} f_k\left(\frac{\lambda\sin y}{n\pi}\right)y\,dy.$$

Since we are interested only in the general character of the λ dependence, we limit ourselves to a rough estimate. It is obvious that in each of the series, the number of significant terms is $n\sim\lambda/\pi$. On the other hand, at $n\ll\lambda/\pi$, we have

$$\int_0^{\pi/2} f_k\left(\frac{\lambda\sin y}{n\pi}\right)dy\cong\frac{n\pi}{\lambda}\int_0^{\infty}f_k(y)\,dy,$$

$$\int_0^{\pi/2} f_k\left(\frac{\lambda\sin y}{n\pi}\right)y\,dy\cong\left(\frac{n\pi}{\lambda}\right)^2\int_0^{\infty}f_k(y)\,y\,dy.$$

Therefore

$$F_{2k}(\lambda)\sim\sum_{n=1}^{\lambda/\pi}\frac{n\pi}{\lambda}\sim\lambda,$$

$$F_{2k+1}(\lambda)\sim\sum_{n=1}^{\lambda/\pi}\frac{(-1)^n}{\lambda^2}n\pi\sim\frac{1}{\lambda}.$$

2. In the study of (3) we encounter another integral:

$$\Phi_k(\lambda)=\int_0^{\infty}\frac{\sin x}{x}f_k\left(\lambda\frac{\sin x}{x}\right)$$

as $\lambda\to\infty$. Proceeding as in the study of $F_k(\lambda)$, we have

$$\Phi_k(\lambda)\cong[1+(-1)^{k+1}]\sum_{n=1}^{\infty}\frac{1}{n\pi}\int_0^{\pi/2} f_k\left(\lambda\frac{\sin y}{n\pi}\right)\sin y\,dy$$

$$+[1+(-1)^k]\sum_{n=1}^{\infty}\frac{(-1)^n}{(n\pi)^2}\frac{\partial}{\partial\lambda}\lambda\int_0^{\pi/2} f_k\left(\lambda\frac{\sin y}{n\pi}\right)y\sin y\,dy.$$

In the derivation of this formula, it has been assumed that the fundamental contribution to the second sum is made by terms with $n\gg1$. In both sums, only terms with $n\lesssim\lambda/\pi$ are important. On the other hand, at $n\ll\lambda/\pi$, we have

$$\int_0^{\pi/2} f_k\left(\lambda\frac{\sin y}{n\pi}\right)\sin y\,dy\sim\left(\frac{n\pi}{\lambda}\right)^2\int_0^{\infty}f_k(y)\,y\,dy,$$

$$\int_0^{\pi/2} f_k\left(\lambda\frac{\sin y}{n\pi}\right)y\sin y\,dy\sim\int_0 f_k\left(\frac{\lambda y}{n\pi}\right)y^2\,dy$$

$$\sim\frac{1}{(2\pi)^{1/2}}\left(\frac{n\pi}{\lambda}\right)^3\int_0^{(\lambda/2\pi)^2}e^{iau}\cos\left(u^{1/2}-\frac{k\pi}{2}-\frac{\pi}{4}\right)u^{1/4}du\sim\left(\frac{n\pi}{\lambda}\right)^{5/2}.$$

As a result,

$$\Phi_{2k+1}(\lambda)\sim\sum_{n=1}^{\lambda/\pi}\frac{n\pi}{\lambda^2}\sim\lambda^0,$$

$$\Phi_{2k}(\lambda)\sim\sum_{n=1}^{\lambda/\pi}\frac{(-1)^n(n\pi)^{1/2}}{\lambda^{5/2}}\sim\frac{1}{\lambda^2}.$$

[1] The attenuation of the sound was not taken into account in Ref. 3, and the expression for A_{2e} which appears there is obtained from (1) in the case $\Gamma\to0$.

[2] It should be noted that T_2 increased upon increase in the field intensity. Within the framework of existing theory, the dependence of T_2 on the field can be attributed to the dependence of the damping of the nonlinear oscillator on the amplitude of its oscillations. The fact that T_2 increases is determined by the choice of the anharmonicity constants.

[3] In calculation of the shape of the pulse echo, allowance for the actual form of $n(\omega)$ leads to only a small distortion.

[1] S. N. Popov and N. N. Kraĭnik, Fiz. Tverd. Tela (Leningrad) 12, 3022 (1970) [Sov. Phys. Solid State 12, 2446 (1970)].

[2] A. R. Kessel', I. A. Safin and A. M. Gol'dman, Fiz. Tverd. Tela (Leningrad) 12, 3070 (1970) [Sov. Phys. Solid State 12, 2488 (1970)].

[3] B. D. Laikhtman, Fiz. Tverd. Tela (Leningrad) 17, 3278 (1975); 18, 612 (1976) [Sov. Phys. Solid State 17, 2154 (1975); 18, 357 (1976)].

[4] A. R. Kessel', S. A. Zel'dovich and I. L. Gurevich, Fiz. Tverd. Tela (Leningrad) 18, 826 (1976) [Sov. Phys. Solid State 18, 473 (1976)].

[5] S. N. Popov, N. N. Kraĭnik and G. A. Smolenskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 21, 543 (1975) [JETP Lett. 21, 253 (1975)].

[6] S. N. Popov, N. N. Kraĭnik and G. A. Smolenskiĭ, Zh. Eksp. Teor. Fiz. 69, 974 (1975) [Sov. Phys. JETP 42, 494 (1975)].

[7] V. M. Berezov, Ya. Ya. Asadulin, V. D. Korepanov and V. S. Romanov, Zh. Eksp. Teor. Fiz. 69, 1674 (1975) [Sov. Phys. JETP 42, 851 (1975)].

[8] Ya. Ya. Asadullin, V. M. Berezov, V. D. Korepanov and V. S. Romanov, Pis'ma Zh. Eksp. Teor. Fiz. 22, 285 (1975) [JETP Lett. 22, 132 (1975)].

[9] B. D. Laĭkhtman, Zh. Eksp. Teor. Fiz. 70, 1872 (1976) [Sov. Phys. JETP 43, 974 (1976)].

[10] N. S. Shiren, and R. I. Melcher, Proc. 1974 Ultrasonics Sym. IEEE, New York, pp. 572-582.

[11]G. A. Smolenskiĭ, N. N. Kraĭnik, V. V. Lemanov and S. N. Popov, Izv. Akad. Nauk SSSR, Ser. Fiz., 39, 965 (1975).
[12]G. A. Smolensky, N. N. Kraĭnik, S. N. Popov and B. D. Laĭkhtman, Ferroelectrics 14, 571 (1976).
[13]Ch. Frénois, J. Joffrin and A. Levelut, J. de Phys. 37, 275 (1976).
[14]B. M. Berezov, Ya. Ya. Asadullin, V. D. Korepanov and V. S. Romanov, Fiz. Tverd. Tela (Leningrad) 18, 180 (1976) [Sov. Phys. Solid State 18, 103 (1976)].
[15]W. H. Kegel and R. W. Gould, Phys. Lett. 19, 531 (1965).
[16]Ch. Frénois, J. Joffrin and A. Levelut, Comp. Rand. Acad. Sci. B278, 57 (1974).
[17]N. S. Shiren, R. L. Melcher, D. K. Garrod and T. G. Kazyaka, Phys. Rev. Lett. 31, 819 (1973).
[18]A. A. Chaban, Fiz. Tverd. Tela (Leningrad) 18, 383 (1976) [Sov. Phys. Solid State 18, 223 (1976)].
[19]A. A. Chaban, Pis'ma Zh. Eksp. Teor. Fiz. 15, 108 (1972) [JETP Lett. 15, 74 (1972)].
[20]A. A. Chaban, Pis'ma Zh. Eksp. Teor. Fiz. 23, 389 (1976) [JETP Lett. 23, 350 (1976)].
[21]R. L. Melcher and N. S. Shiren, Phys. Rev. Lett. 36, 888 (1976).

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Increase of the Curie temperature of the magnetic semiconductor EuO

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The possibilities are considered of greatly increasing the Curie temperature of ferromagnetic solid solutions based on europium monoxide while preserving the semiconducting character of their conductivity. The experimental results of this study attest to the existence of magnetic heterogeneity in homogeneous EuO–SmO solid solutions. The discussion is carried out within the framework of the magnetic impurity state and direct excited exchange models. It is suggested that the exchange interactions are switched in the investigated solid solutions in "relay" fashion.

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From among the ferromagnetic semiconductors, particular interest attaches to divalent europium chalcogenides EuX (X = O, S, Se, Te), which are characterized by a number of unusual properties.[1] The simplicity of the crystal (and magnetic) structure (of the NaCl type) makes them convenient model objects in the theory of ferromagnetism.[2] The practical utilization of such materials is limited to the low magnetic-order temperatures—the Curie points of EuS and EuO are respectively 16 and ≈ 70 K. The problem of increasing T_C in these ferromagnetic semiconductors while preserving their semiconductor conductivity is therefore quite pressing.

It is known that T_C of EuO can be increased by hydrostatic compression of the crystals or by the presence of excess europium atoms in them.[3] Another way of solving this problem, by doping EuO (or EuS) with ions of trivalent rare-earth metals (REM),[4] also ensures a substantial increase of the Curie temperature (almost double in the oxides). In these cases, however, the increase of T_C is accompanied by an appreciable decrease of the activation energy of the conductivity (of the f–d transition energy), by an increase of the density of the carriers in the d band, and by an abrupt increase of the conductivity, to values $\sigma \approx 10^2 - 10^3$ (Ω-cm)$^{-1}$.[5]

The magnetic, electric, optical, and some other properties of europium chalcogenides doped with trivalent REM, such as La or Gd, can be explained within the framework of the model of magnetic impurity states,[6,7] according to which, the excess valence electron of the impurity is localized near the impurity atom as a result of the Coulomb interaction. Stabilization of the system and the minimum of its free energy are attained as a result of the strong i–f exchange interaction between the impurity electron and the $4f$-spins of the twelve nearest magnetic ions of europium. As a result, a magnetic quasimolecule is formed, characterized by a gigantic magnetic moment which is ascribed to its central ion. The onset of such a quasimolecule is accompanied by the appearance of an unusual magnetic contribution to the specific heat in the region of the Curie temperature, as was observed, for example, when EuS was doped also with gadolinium.[8] At the same time, an anomalously large increase of the ferromagnetic susceptibility takes place at $T \geqslant T_C$, leading to a positive deviation from the Curie-Weiss law.[9] It follows from the foregoing that the solution of the problem of increasing T_C of ferromagnetic semiconductors, besides being of practical importance, calls for the development of premises concerning the properties of the magnetic quasimolecules they contain. The experimental study of the latter has not yet found its due reflection in the literature.

Samokhvalov *et al.*[10] were the first to observe an

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