Echo Phenomena in Piezoelectric Crystals

N. S. Shiren, R. L. Melcher, D. K. Garrod, and T. G. Kazyaka
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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We report an extensive set of experimental measurements on electric-field echoes in insulating and semi-insulating crystals. Previously suggested mechanisms cannot explain the results. In particular, three-pulse echoes with decay times T_1 of several hours have been observed at low temperatures in semi-insulating II-VI compounds. We propose a mechanism based upon the redistribution of trapped electronic space charge.

The simultaneous discovery by two groups of an anomalous echo phenomenon in several ferroelectric materials[1,2] has stimulated considerable experimental and theoretical activity.[3] Various mechanisms have been proposed, some of which may be treated in a general formalism analogous to spin echoes.[3] Several mechanisms (including ours) have in common that a forward-propagating strain wave of frequency ω and wave vector $\vec{k}$, $(\omega, \vec{k})$, interacts with an electric field of either $(\omega, 0)$ or $(2\omega, 0)$ to produce a backward-propagating strain wave $(\omega, -\vec{k})$. However, previous models have assumed that the interactions are characteristic of pure crystals. In this Letter we report an extensive series of experiments whose results cannot be reconciled with the latter viewpoint, nor treated by a spin-echo formalism. Our low-temperature results are consistent with a mechanism based upon the redistribution of electronic space charge caused by electric-field–induced quantum-mechanical tunneling from shallow electron traps (or by other field-dependent detrapping mechanisms). The redistributed charge varies spatially on a scale of the acoustic wavelength; i.e., charge gratings are formed and may be stored for long time periods. This mechanism bears similarities to the acoustoelectric aftereffect,[4] charge-transfer optical holographic storage,[5] and dc persistent internal polarization.

The extreme variability of the results among crystals of the same compound obtained from different sources indicates that the echo phenomena are associated with the presence of defects. We have observed the echoes in several polar materials including CdSe, CdS, ZnO, $LiTaO_3$, $LiNbO_3$, and SbSI, and also in nonpolar CdTe (T_d symmetry), showing that the previously supposed necessity of polar crystals is invalid. However, except where otherwise specified, all the experimental results discussed below were obtained from a single sample of high-resistivity [$\rho(300°K) \approx 10^{11}$ Ω cm], photosensitive, sulfur-compensated CdS. Both a- and c-cut single-crystal rods and plates were placed in the electric-field regions of re-entrant or rectangular X-band cavities ($\omega/2\pi \simeq 9$ GHz) or between the parallel plates of a capacitor ($\omega/2\pi \simeq 50$–700 MHz). No significant anisotropy of the results was detected for CdS. At low frequency ($\omega/2\pi \lesssim 500$ MHz), echoes were observed from 1.4 to 300°K whereas at X-band frequencies the measurements were restricted to below 70°K. The echo phenomenon manifests itself in three basic types of electric-field signals, all of which are shown for CdTe in Fig. 1: (a) The "aftereffect" is a signal of width 2Δ observed during and immediately following a strong applied electric-field pulse of width Δ. A stimulated aftereffect can be observed during and immediately following a weak pulse applied at a la-

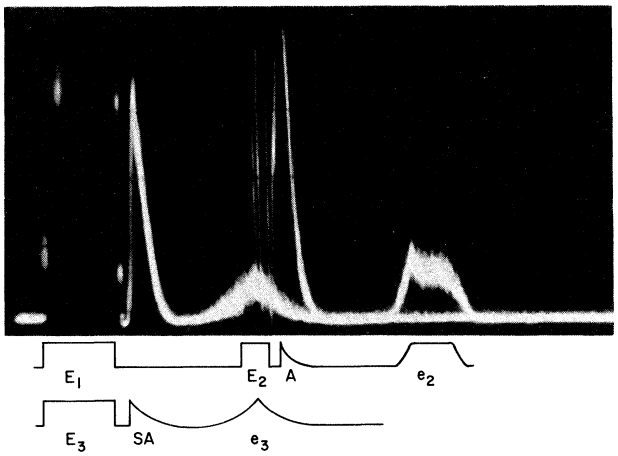

FIG. 1. X-band signals in CdTe at 4.2°K. Superposition of scope traces from a repetitive sequence in which one magnetron, pulsed each repetition period at low power, is used for both first (E_1) and third (E_3) pulses, while another, pulsed every other period at high power, is used for the second pulse (E_2). e_2 and e_3 are two- and three-pulse echoes, respectively; A and SA are, respectively, the tails of the aftereffect and stimulated aftereffect, following a receiver dead time after the initiating pulses.

ter time. The aftereffect is distinct from the piezoelectric "ringing" of the crystal. (b) The "two-pulse echo" occurs at time $t = 2\tau$ following two pulses applied at $t = 0$ and $t = \tau$. The amplitude of this echo decays as $\exp(-2\tau/T_2)$, where T_2 is a characteristic time. (c) The "three-pulse echo" occurs at time $t = T + \tau$ following three pulses applied at $t = 0$, $t = \tau$, and $t = T$. The amplitude of this echo decays as $\exp(-2\tau/T_2 - T/T_1)$, where T_1 is another characteristic time. The seven points listed below record our principal experimental findings concerning these phenomena.

(1) The amplitudes of the observed signals were sharply dependent upon the illumination of the sample with visible light. With the crystal in thermal equilibrium in the dark, no signals were observed. During and immediately following illumination with white light, strong echoes (signal-to-noise ratio approximately 40 dB in this sample of CdS) could be generated. The decay time for generation in the dark, T_T, varied from less than a second at 300°K, to ≈ 30 sec at 77.4°K, to at least a day at 4.2°K.

(2) The time constant for the decay of the stimulated aftereffect and the T_1 decay of the three-pulse echo were measured to be several hours at liquid-helium temperatures in the dark.[7] (In the presence of illumination, T_1 decreased to the order of 1 sec.) The decay was nonexponential, indicating a distribution of T_1's. There was no significant dependence of T_1 on frequency. As the intensity of the three-pulse echo was varied by adjusting various experimental parameters, T_1 was found to increase with increased echo amplitude. T_1 decreased with increasing temperatures, and for $T \gtrsim 25$°K no three-pulse echo or stimulated aftereffect was observed. Any model in which T_1 is to be interpreted as a phonon relaxation time[3] is clearly inapplicable to the present data. Three-pulse echoes with long T_1's were observed only in anion-compensated II-VI semiconductors.

(3) Signal amplitudes were strongly dependent on the wavelength λ of the illuminating radiation, as shown in Fig. 2. The data have been corrected for changes in echo amplitude caused by the dependence of T_2 on λ, as is also shown in Fig. 2. Similar data were obtained at lower temperatures with, however, somewhat greater uncertainty because of the hysteresis time T_T following illumination, as discussed in point (1) above. The band gap of CdS at 300°K is approximately 2.4 eV, corresponding to $\lambda_{gap} \approx 5100$ Å. The apparent peak in

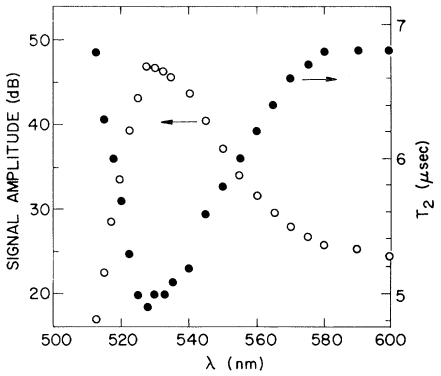

FIG. 2. Two-pulse–echo signal amplitude (open circles) and T_2 (closed circles) in CdS versus wavelength of illuminating radiation: $T = 298$°K, $\omega/2\pi = 220$ MHz. The data are uncorrected for optical absorption.

the echo amplitude, the minimum in T_2, and the peak in the ultrasonic attenuation (not shown here) all occur at or just below the band gap.

(4) From measurements as a function of light intensity, light wavelength, temperature, and frequency, there is a qualitative correlation of the ultrasonic attenuation with T_2^{-1}. T_2 typically ranged from 1 to 12 μsec. However, at $T \simeq 25$°K after illumination, and with the crystal in the dark, T_2's as long as 35 μsec were observed at $100 < \omega/2\pi < 700$ MHz. Under the same conditions, separate measurements showed that the ultrasonic attenuation of piezoactive acoustic modes reached a minimum at this temperature. Similarly, the photodielectric effect exhibited a sharp decrease when this temperature was approached from below.

(5) The two-pulse–echo amplitude depends on the amplitudes of the two input pulses as shown in Fig. 3. For $E_1 < E_2$ the echo amplitude increases linearly with E_1 over a rather broad range, peaking at $E_1 \approx E_2$, and declining sharply for $E_1 > E_2$. As a function of E_2 the echo amplitude is sharply peaked and shows no simple power-law behavior over any extended range of E_2. The position of the peak in the echo amplitude as a function of E_2 is unaffected by the magnitude of E_1 for E_1 less than E_2 at the peak. For E_1 greater than that value, the peak occurs at $E_2 \approx E_1$. This behavior was observed in all materials for which field dependences were measured in detail.

(6) The application of dc electric fields of the order of 10^4 V/cm simultaneously with the rf pulses was found to decrease the amplitude of the two-pulse echo monotonically. Also, stored signals could be destroyed by large rf electric

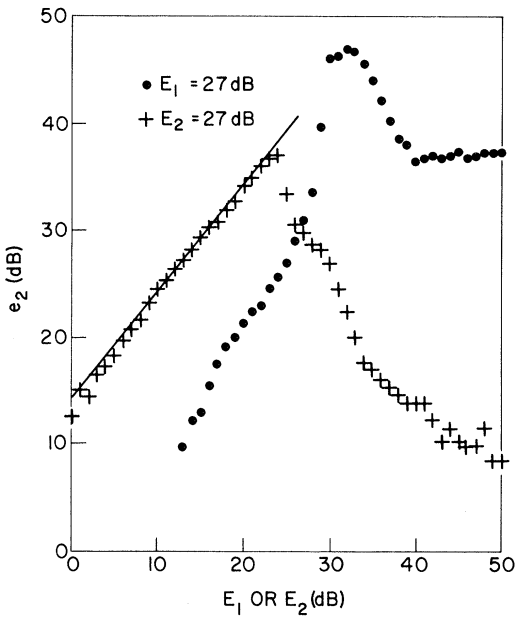

FIG. 3. Relative two-pulse–echo amplitudes e_2 as a function of relative input electric fields E_1 or E_2 in CdS at 4.2°K and at $\omega/2\pi \approx 9$ GHz. Crosses, e_2 versus E_1; closed circles, e_2 versus E_2; solid line, $e_2 \propto E$.

fields.

(7) Two cavity experiments were performed in which a forward propagating strain wave at $(\omega, \vec{k})$ interacted with an electric field at frequency ω or 2ω to produce a backward wave at $(\omega, -\vec{k})$. In the presence of illumination the backward wave produced by the ω field increased in amplitude, whereas the backward wave produced by the 2ω field decreased. Therefore, the interaction of $(\omega, \vec{k})$ phonons with a 2ω field as discussed by Thompson and Quate[8] is distinct from the echo phenomena discussed in this paper, which involve the interaction of $(\omega, \vec{k})$ phonons with an ω field.

We believe the low-temperature experimental observations can be explained on the basis of the following model. Illumination of the sample causes the filling of shallow ($\epsilon_T \approx 10^{-2}$ eV) electron traps near the conduction band. Band-gap or nearly band-gap radiation is required for this, in agreement with data shown in Fig. 2. Such traps can have lifetimes of days at liquid-helium temperatures. Therefore, the time T_T for echo formation after illumination [see point (1) above] is to be associated with the trap lifetime. In the formation of a three-pulse echo the first pulse generates $(\omega, \vec{k})$ phonons via the piezoelectric effect. During the second pulse the total electric field in the crystal is the sum of the piezoelectric field of the phonons generated by the first pulse and the applied field of the second pulse. The probability for field-induced tunneling from trapping states is a function of the absolute magnitude of this total electric field[9] and, therefore, contains a term which is time independent but varies spatially as $\cos(\vec{k}\cdot\vec{r})$. This tunneling probability then leads to an inhomogeneous trapped electronic space-charge grating. The electric field of the third pulse acts on the grating to generate a backward propagating wave (as well as a forward wave) which is detected piezoelectrically at the crystal surface. In addition, when acted upon by the forward-propagating wave piezoelectrically generated at the crystal surface by the third pulse, the grating generates a uniform electric field. The echo is the sum of these two outputs which occur simultaneously. Both the aftereffect and the two-pulse echo can be explained in this way with an appropriate combination of rf electric fields and propagating piezoactive strain waves.

On the basis of this model, the decay time T_2 is interpreted as a phonon inelastic scattering lifetime. The time constant T_1, which is interpreted as the lifetime of the inhomogeneous trapped charge grating, is less than the lifetime T_T of the uniformly distributed trapping states. This is a consequence of the inhomogeneous space-charge field of the grating.[6]

Because of the nature of the tunneling probability, the echo amplitude is an extremely nonlinear function of the pulse amplitudes E_1 and E_2. However, by assuming a distribution of trap depths, the behavior shown in Fig. 3 and discussed in point (5) above, can, at least qualitatively, be explained on the basis of this model.

In addition, we have considered two dynamic mechanisms which give rise to an aftereffect and a two-pulse echo without the formation of a stored charge grating. These are based upon (1) the detrapping caused by the applied rf electric field alone, and (2) the acoustoelectric aftereffect[4] associated with conduction electrons. All three mechanisms may be operative. Under conditions in which no three-pulse echo is observed, only the dynamic mechanisms can be present; which of them dominates will depend upon the photoconductivity and temperature. We believe that these mechanisms based upon impurities explain all the reported results on echo phenomena in II-VI compounds and probably also in other materials. A more detailed analysis will be published separate-

ly along with the results of other experiments.

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Low-Temperature Thermal Brillouin Scattering in Fused Silica and Borosilicate Glass*

W. F. Love

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

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Brillouin scattering experiments have been performed between 1.7 and 300 K in glasses to demonstrate the existence of thermal phonons. The theoretically expected linear temperature dependence of the Brillouin peak intensities has been observed.

In crystalline solids, the existence of Debye thermal lattice excitations or phonons can be demonstrated convincingly through specific-heat measurements. It is well established that the low-temperature lattice specific heat of pure crystals agrees to within percents with that calculated on the basis of the Debye model, using experimental sound velocities. In noncrystalline dielectric solids, however, it has recently been shown that the low-temperature specific heat C_v does not obey the Debye law.[1-2] Instead, it was found that C_v can be expressed as a polynomial,

$$C_v = c_1 T + c_3 T^3, \tag{1}$$

where c_3 is up to twice as large as predicted by the Debye model. This observation has given rise to the fundamental question whether Debye-like plane-wave thermal excitations exist at all in glasses at low temperatures, i.e., whether one is justified in writing

$$C_v = c_1 T + (c_3' + c_{\mathrm{Debye}}) T^3, \tag{2}$$

where both $c_1 T$ and $c_3' T^3$ are caused by the disorder. The question had arisen in connection with a study of the thermal conductivity in glasses, in which the possibility had been discussed that the heat was not carried by Debye phonons.[1,2] As an alternative, it had been suggested that the phonon lifetimes could be so short that a separation of c_3 as written in Eq. (2) would not be justified. Recent low-temperature (0.1 to 1 K) ultrasonic attenuation measurements in the frequency range of 10^9 sec^{-1} have not been able to answer this question.[3,4] Rather, it was found that the attenuation increased with decreasing pulse intensity, demonstrating strong nonlinear forces in the glassy solid. From these measurements, an extrapolation to ultrasonic intensities characteristic for thermal phonons was not possible.

In this Letter, we want to present experimental evidence that thermal phonons in the frequency range of 2×10^{10} sec^{-1} do indeed exist in glasses in the temperature range 1.7 to 300 K, and that their lifetimes are at least 10 vibrational periods. Earlier spontaneous Brillouin scattering experiments in glasses were done at temperatures

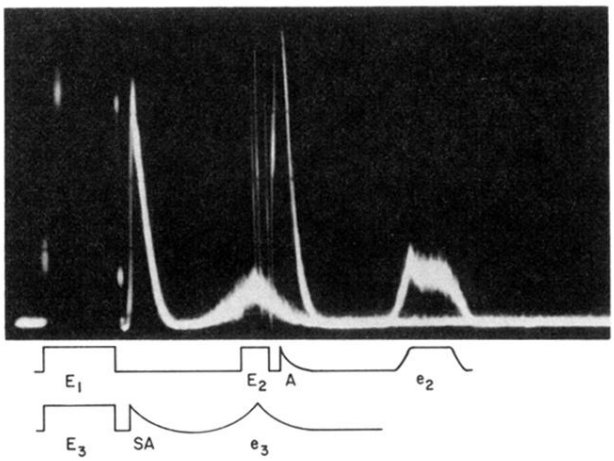

FIG. 1. *X*-band signals in CdTe at 4.2°K. Superposition of scope traces from a repetitive sequence in which one magnetron, pulsed each repetition period at low power, is used for both first (E_1) and third (E_3) pulses, while another, pulsed every other period at high power, is used for the second pulse (E_2). e_2 and e_3 are two- and three-pulse echoes, respectively; A and SA are, respectively, the tails of the aftereffect and stimulated aftereffect, following a receiver dead time after the initiating pulses.