Backward-Wave Phonon Echoes in Glass

N. S. Shiren, W. Arnold,[a] and T. G. Kazyaka
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Backward-wave phonon echoes (polarization echoes), heretofore only observed in piezoelectric crystals, were generated in several different glasses. Echo amplitudes were found to be proportional to the number of unassociated hydroxyl ions in the samples. It is proposed that OH^- ions in glass form a distribution of inhomogeneously broadened resonances, sensitive to both ultrasonics and electromagnetic fields. Effect of this conjecture on other measurements in glasses are discussed, as are various measured properties of the echoes.

We report the observation of backward-wave phonon echoes in several glasses: As_2S_3 Pyrex, Suprasil 1, Suprasil 2, Borosilicate glass (BK-7), and fused SiO_2 (equivalent to Suprasil W). Measurements were made at the frequency $\omega/2\pi \simeq 9$ GHz and at temperatures $T \geqslant 1.25$ K, using input pulses of width 100 to 400 ns. Two-pulse echoes were detected only when the first pulse was an ultrasonic wave and the second a standing-wave electric field. Stimulated (three-pulse) echoes were not observed under any condition. The effect is thus similar to parametric polarization echoes[1] (also variously termed electric-field echoes, phonon echoes, boson echoes) observed in bulk piezoelectric crystals, but this is the first observation of the phenomenon in nonpiezoelectric materials as well as in noncrystalline materials. Based on the results and their interpretation, we expect that echoes should be observable in many nonpiezoelectric materials, both crystalline and amorphous.

In most experiments the samples were coated with a paint consisting of ZnO powder (Fischer Z-52) in glyptal varnish (GE7031), and placed in the electric-field region of either a re-entrant or rectangular cavity. The paint serves as a spatially incoherent ultrasonic transducer. Since echoes can be generated in loose ZnO powder,[2] although completely damped even by liquid He, the paint was tested by coating it on the ends of a Z-cut crystal quartz rod; no echoes were observed. (Phonon echoes cannot be generated in pure α-quartz.) They were also not observed in glass samples which were uncoated, showing that ultrasonic waves are necessary to formation of the echo. As a further check a double-ended (two-cavity) experiment was conducted on a Pyrex rod with polished faces, bonded to an x-cut quartz transducer, with the latter in a re-entrant cavity and the Pyrex in the electric-field region of a rectangular cavity. The backward-propagating echo was detected in the re-entrant cavity only when the first input pulse launched an ultrasonic wave in the transducer and the second pulse was applied to the rectangular cavity, timed to coincide with the propagating pulse in the Pyrex. Echoes were not observed with both input pulses applied to the same cavity resonator.[3]

As is also the case in piezoelectrics, we find that the nonlinearity is associated with the presence of impurities, in the present case with OH^-. In Fig. 1 we have plotted the echo amplitude, e_2, versus OH^- content for twelve different glass samples. The amplitude is proportional to the number of unassociated OH^- ions contained in the cavity resonator, over a range of two orders of magnitude in concentration, as measured by infrared absorption at 2.7 μm. The infrared data were reduced utilizing the oscillator strength of OH^- in SiO_2 as given by Hetherington and Jack[4]

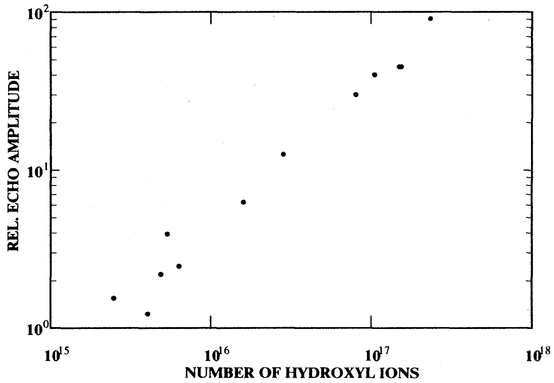

FIG. 1. Echo amplitudes, e_2, vs number of hydroxyl ions for twelve different glass samples. In order of increasing number: As_2S_3 (Servocorp), As_2S_3 (Ealing), fused SiO_2, As_2S_3 (Ealing), As_2S_3 (Servocorp), vitreous silica, vitreous silica, Pyrex, Suprasil 2, Pyrex, Pyrex, BK-7.

for all samples except Pyrex and BK-7. For these the oscillator strength reported by Müller-Warmuth *et al.*[5] was used. From the data and the observed signal/noise ratio, we calculate a minimum detectable number of OH$^-$ ions at 1.25 K, $N \simeq 10^{14}$, by this technique. The amplitudes given in Fig. 1 are those measured at the fixed input-pulse separation, $\tau = 800$ ns, and are not extrapolations to $\tau = 0$. We have presented the data in this manner because the echo decays are not exponential in τ for small τ; and, therefore, in order to make an extrapolation a quantitative theory of the decay is necessary. For large pulse separations, τ, the decay is exponential, $e^{-b\tau}$, and is expected to be proportional to the ultrasonic attenuation. We have measured the temperature dependence of b in both As$_2$S$_3$ and BK-7 and find $b \propto T^{1.8}$ in the temperature range $1.25\ \text{K} \leq T \leq 2.0$ K. Above 2 K, b increases more rapidly, approaching $T^{2.2}$ in As$_2$S$_3$, and $T^{2.7}$ in BK-7 at 4 K. The temperature dependence agrees with that expected for ultrasonic attenuation due to a combination of saturable resonance absorption (decreasing with T) and relaxation absorption (increasing with T) by the intrinsic two-level systems, as reported in the literature.[6] We expect the resonance part of the attenuation to affect the generated backward wave only, since in these experiments the forward wave launched by the first input pulse is strong enough to saturate completely the resonance absorption. In many (but not all) cases this is all that is required to explain the non-exponential echo decay envelope.

The dependences of the echo amplitude on input-pulse powers cannot be similarly explained. In Fig. 2 we show the variation in As$_2$S$_3$ of the echo amplitude, e_2, versus S, the relative strain amplitude of the first pulse, and also versus E, the relative electric field of the second pulse. At low input powers e_2 varies approximately as S, but reaches a peak and folds over with increasing S. We have also observed that the value of S at which e_2 peaks increases with increasing E. As a function of E, e_2 at first increases approximately as $E^{1.3}$ and then flattens off. In BK-7 and Pyrex the signal/noise ratio was greater and we were able to establish that $e_2 \propto E^2$ for small E and S.

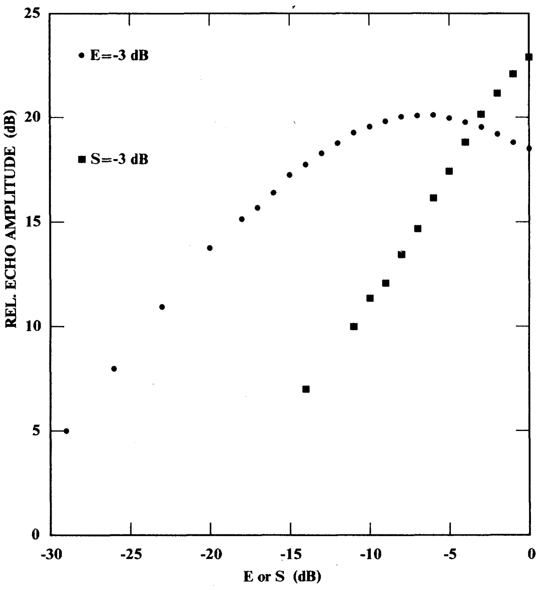

FIG. 2. Relative echo amplitudes, e_2, in As$_2$S$_3$, vs relative strain, S, of the first input pulse (circles), and vs relative electric field, E, of the second input pulse (squares).

Backward-wave echo generation may be considered as a four-wave parametric process for which the simplest source is a sixth-rank-tensor Hamiltonian,[7] $\mathcal{H} \propto E^2S^2$, producing a nonlinear electroelastic stress $T^{\text{NL}} \propto E^2S$. However, in the present case, the data of Fig. 2 indicate a more complex form for T^{NL}. From the known behavior of OH$^-$ in alkali halides,[8] it is reasonable to assume that an unassociated hydroxyl ion in glass forms a multilevel system with inhomogeneously broadened transitions lying in the microwave spectrum. Transitions can be induced by photons and by phonons. Both resonant and relaxation-type absorption and dispersion contain nonlinear terms which can produce the desired stress. As a simple example, a straightforward density-matrix calculation for a two-level spin-type Hamiltonian subjected simultaneously to an oscillating electric field, $\vec{E} = \vec{E}_0 \cos(\omega t + \theta)$, and a forward-propagating ultrasonic strain, $S = S_0 \cos(\omega t - kx)$, yields for the imaginary part of the generated stress,

$$T^{\text{NL}} = \frac{\gamma_S \hbar(\gamma_E E_0 e^{i\psi} + \gamma_S S_0 e^{-ikx}) N_{\text{OH}} T_2^*}{[1 + T_1 T_2(\gamma_E^2 E_0^2 + \gamma_S^2 S_0^2 + 2\gamma_E \gamma_S E_0 S_0 \cos(kx+\psi)]^{1/2}} e^{i\omega t} + \text{c.c.}, \tag{1}$$

where $\psi = \theta + \varphi_E - \varphi_S$, $\hbar\gamma_E e^{i\varphi_E}$ is a complex transition dipole moment, $\hbar\gamma_S e^{i\varphi_S}$ is a complex electro-elastic-coupling constant for this transition, N_{OH} is the equilibrium population difference per cubic centimeter, T_1 and T_2 are longitudinal and transverse relaxation times assumed short compared with the pulse width. In Eq. (1) we have already integrated over the inhomogeneity, assumed flat and of width $T_2{}^{*-1}$.

If $T^{\rm NL}$ is expanded as a Fourier series in e^{imkx} (with $m=0, \pm 1, \pm 2, \ldots$), the inhomogeneous stress in the backward-wave equation is given by the $m=+1$ component. While this can be only a rough approximation to the true multilevel system, its dependences on E and S are qualitatively similar to the data. The $m=-1$ component is a source term for resonant attenuation or amplification of the forward wave; however, we expect this to be small compared with attenuation by the intrinsic absorbers because of the low concentration of OH^-.

The assumption of two different two-level systems, only one of which, OH^-, couples to electromagnetic fields, also helps explain several other results previously reported in the literature: (1) Electromagnetic saturation of the ultrasonic absorption is not observed in water-free samples.[9] However, saturation of the ultrasonic absorption by microwaves in samples containing water[10] can be explained if one assumes that the observed saturation of the intrinsic two-level systems occurs through cross-relaxation or hot-phonon emission from the electromagnetically saturated OH^- systems. (2) The unsaturated ultrasonic absorption is independent of OH concentration[6] because the latter is always small compared with the number of intrinsic absorbers. (3) OH does not contribute to the thermal resistivity.[11] If one assumes the inhomogeneous linewidth of the OH absorbers to be less than that of the intrinsic ones, then this is explained by an argument due to Berman, Brock, and Huntley[12] and utilized by McClintock *et al.*[13] to explain certain anomalies in the thermal conductivity of paramagnets.

Finally, we wish to point out that although $T^{\rm NL}$ can be derived from a resonance interaction, the echo process is different from that of the forward-propagating echoes in glass reported by Golding and Graebner[14] and also from the backward and forward echoes in paramagnets reported by Shiren and Kazyaka.[15] In these experiments, the resonance relaxation times, T_1 and T_2, are long compared with the pulse widths and stimulated echoes are observable. The motion of the coherent nonlinear stress is time reversed by the second pulse; for the backward echo, time reversal also occurs in the phonon field. In the present case, and for polarization echoes in general, the backward waves are generated in a parametric simultaneous four-wave interaction. Stimulated echoes cannot be generated because the motion of $T^{\rm NL}$ is rapidly damped following each pulse. Time reversal is manifested only in the generated phonon field, as wave-vector reversal.

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(a) IBM World Trade Postdoctoral Fellow. Permanent address: Max-Planck-Institut für Festkörperforschung, 7 Stuttgart, Büsnauerstrasse, Federal Republic of Germany.

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Correlation Crystal Fields for Lanthanide Ions

B. R. Judd
Physics Department, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 3 June 1977)

To reduce the discrepancies in the crystal-field analyses of the electronic configurations $4f^N$ of lanthanide ions, it is argued that each component $(C_q^{(k)})_i$ of the single-electron tensor $C^{(k)}$ for electron i occurring in the conventional crystal-field Hamiltonian should be augmented to $c_k(\vec{s}\cdot\vec{s}_i)(C_q^{(k)})_i$. Parameters c_k of the order of -0.1 lead to significant improvements in the fit with a wide variety of experimental data.

A well-established procedure is available for calculating the energy levels deriving from the electronic configuration $4f^N$ of lanthanide ions situated in crystal lattices.[1] The crystal-field Hamiltonian H is written down as a sum of single-electron tensor operators $(C_q^{(k)})_i$ with parameters B_q^k as coefficients. Considerations of parity, of angular-momentum selection rules, and of site symmetry serve to reduce the terms in H to a manageable number. For C_{3h} symmetry, only four are required.[1] In contrast, the available data that depend on them are often very rich and varied. For example, a recent study by Crosswhite *et al.*[2] for Ho^{3+} substituted for La^{3+} in LaCl_3 lists 168 observed crystal-field components arising from 39 free-ion levels. Discrepancies that arise in fitting theory to experiment, although not usually pronounced, have been sufficiently unambiguous to provoke several attempts to improve matters.[3,4] The basic difficulty lies in the large number of parameters that are required to represent the various two-electron operators that can be added to H without violating any symmetry constraints. Thus, Bishton and Newman[3] report that 637 two-electron parameters can be constructed for the lowest site symmetry, while even for octahedral symmetry no fewer than 41 acceptable operators exist.[5]

Rather than attempt a complete parametrization, it seems better to examine the physical origin of the two-electron terms in the augmented Hamiltonian H'. At first sight, this seems a formidable task, particularly when it is recalled that Newman[6] distinguished as many as ten contributions to the single-electron operators in H. Even if the $4f$ electron is assumed to be localized on the lanthanide ion (and thus not subject to the renormalization effects recently considered for actinides[5]), many processes can lead to correlation effects. For example, multipole moments on the ligands induced by electron i in the $4f$ shell interact with another electron j in the $4f$ shell and produce two-electron effects. One feature of this and many other correlations is that the final rank k of such tensorial products as $(C_i^{(t)}C_j^{(p)})^{(k)}$ can run as high as 12. However, Crosswhite *et al.* find that the discrepancies in the case of $\mathrm{Ho}^{3+}\ 4f^{10}$ can be greatly reduced simply by making the single-electron parameters B_q^k term dependent. Evidently tensors for which $k>6$ play a small role. This suggests that the two-electron operators should be produced by contracting products of the type $(C_i^{(t)}\cdot C_j^{(t)})(C_i^{(k)}+C_j^{(k)})$.

A general treatment of these kinds of mechanisms requires many parameters. However, there is one source of such terms that is both physically plausible and comparatively easy to treat analytically. The strong attractive exchange forces between $4f$ electrons whose spins are similarly directed leads to a less-extended radial eigenfunction and hence to smaller B_q^k. The use of variable radial functions, is, of course, a central feature of the spin-unrestricted Hartree-Fock method; to my knowledge, the only calculations for lanthanide ions appear to be made for cases where all $4f$ electrons share the same radial eigenfunction.[7] As far as the two-electron terms in H' go, the most elementary way to introduce them is to take each term $B_q^k(C_q^{(k)})_i$ in H and make the replacement

$$(C_q^{(k)})_i \to c_k(\vec{S}\cdot\vec{s}_i)(C_q^{(k)})_i. \tag{1}$$

The c_k (where $k=2, 4, 6$) are three parameters which must necessarily be negative if the contraction of the radial function is to correspond to similarly directed spins. Since $\vec{S}$ includes $\vec{s}_j$ $(j\neq i)$,