Enhancement of Backward-Wave Phonon Echoes by Structural Defects in Quartz

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The magnitude of backward-wave phonon echoes at 17.3 GHz in α-quartz was found to depend strongly on the presence of structural defects introduced by thermal quenching of the crystal. In addition, the linear dependence of echo magnitudes on both acoustic and microwave powers suggested that the effect of the defects was to introduce large static strains which enhanced the intrinsic mechanisms.

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We have observed that the generation of backward-wave phonon echoes in single crystals of quartz is strongly influenced by the presence of structural defects. We were able to increase or decrease the magnitude of ω-2ω echoes by as much as 23 dB merely by quenching or annealing the specimens. In addition, in one sample after quenching, we were able to generate very small ω-ω echoes, the first time that such echoes have been observed in quartz. Despite the clear correlation of the echoes with defects, the observed, linear, power dependences appeared to indicate that they were being generated by intrinsic mechanisms. We shall suggest a possible resolution of this paradox. One particular importance of these results is that they explain the lack of quantitative reproducibility in other phonon echo experiments performed on supposedly similar materials.

The technique of phonon echoes provides a valuable means of studying lattice nonlinearities in crystals.[1,2] In the ω-2ω system used predominantly in the experiments described here, a piezoelectrically excited acoustic wave at a frequency of 17.27 GHz was mixed with a microwave radiation pump at 34.54 GHz to generate the backward-wave acoustic "echo" at 17.27 GHz. Peak microwave powers of approximately 500 W at 17.27 GHz and 2000 W at 34.54 GHz could be delivered, with respective pulse lengths of 250 and 150 ns. The quartz crystals we used were of the natural Brazilian variety. X-ray fluorescence showed that they contained of the order of a few hundred parts per million of Al, Fe, and Cu with lesser quantities of Ni, Zn, and Sn. The samples were 2-mm-diam cylinders, 15 mm long, with polished faces, both X-cut (longitudinal mode) and AC-cut (transverse) rods being used. They were immersed directly in liquid helium-4 below 2 K in order to minimize acoustic loss.

We found a systematic correlation between the heat treatment of the specimen and the magnitude of the ω-2ω backward-wave echoes that were subsequently observed. The rapid quenching of quartz rods by direct immersion in liquid nitrogen at 77 K resulted in a large increase in echo magnitude. Conversely, annealing the specimens at 425° C for 24 h and cooling them slowly back to room temperature over a further 24 h caused a systematic decrease in generation efficiency. We believe that quenching had the effect of creating a large number of structural defects in the crystals and in some of our samples the gross defects could actually be seen by eye. It is well documented through microwave ultrasonic attenuation studies that thermal cycling to low temperatures results in a gradual degradation of acoustic quality due to increased strain content. Results obtained by a variety of techniques, for instance, thermoluminescence and radioluminescence,[3,4] have demonstrated that annealing and slow cooling of α-quartz reduces the number of lattice vacancies in a single crystal. This is entirely consistent with our observation of a large increase in the number of reflection echoes after annealing. Figure 1 shows the relative changes in magnitude of phonon and reflection echoes that resulted from a single anneal of specimen AC No. 2. A complete summary of the ω-2ω data obtained on all the samples is given in Table I. It can be seen from Table I that, as a general rule, the phonon echo decay time T_2 was decreased by quenching the sample and was increased by annealing. In contrast to the decay determined by acoustic attenuation, the quantity T_2 in phonon echo experiments is sensitive only to irreversible scattering processes. Any elastic process, such as wave-form distortion arising from the spatial variation of lattice properties due simply to strain, acts in reverse for the backward waves and merely reforms the original acoustic pulse without loss. Thus, in our experiments, the changes in T_2 indicated variations in the number of defects producing dissipative scattering of phonons, rather

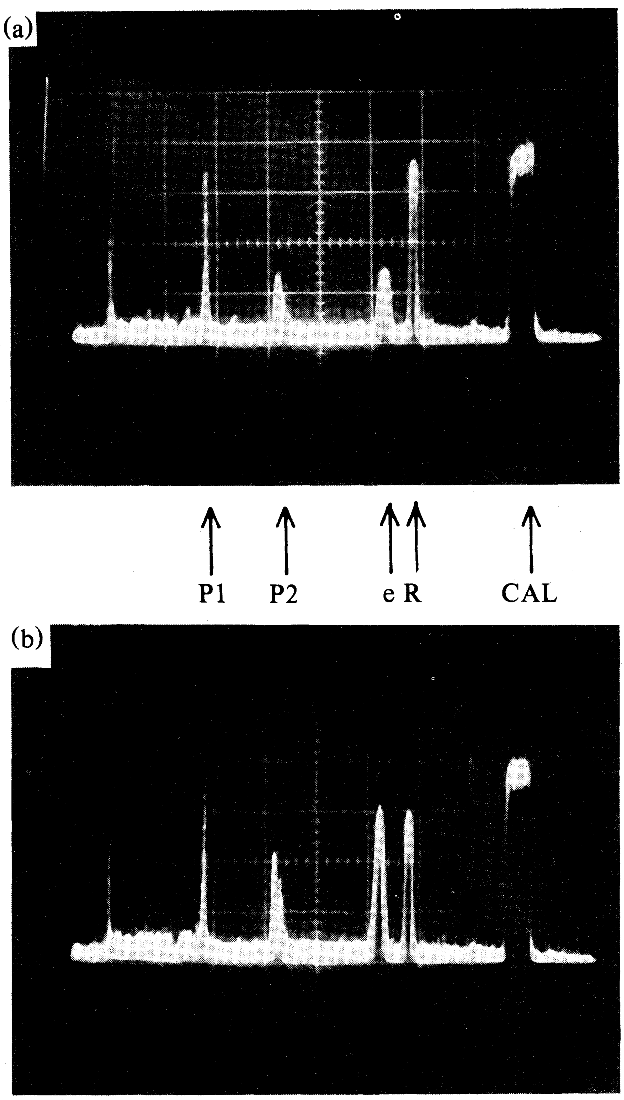

FIG. 1. Relative magnitudes of the phonon echo (e) and the first reflection echo (R) in (a) run 3 and (b) run 4 on AC No. 2. The exciting pulses are at 17.3 GHz (P1) and 34.6 GHz (P2). A calibration pulse (CAL) is supplied direct to the detector from the primary klystron. The horizontal scale is 1 μs cm^{-1}. The phonon echo has increased on quenching by 8 dB while the reflection echo has decreased by 3 dB.

than fluctuations in the magnitude of random strains.

Additional proof that we were observing scattering due to structural defects, and not merely dephasing due to strains, was furnished by the occurrence of a nonexponential ω-2ω echo decay in samples X No. 3 and AC No. 2. Figure 2 shows data taken on X No. 3. Interpreting the data in terms of a power-dependent ultrasonic attenuation, α, we could estimate that α varied between about 0.3 dB cm^{-1} and 0.8 dB cm^{-1}, over a range of input power of about 20 dB. The fact that the higher attenuation occurred at lower intensities suggested the absorption of radiation by saturated two-level systems (TLS). Laermans[5] at 9 GHz, and Rodriguez and Nava[6] at 140–210 MHz, have observed similar ultrasonic attenuation in irradiated quartz that they have attributed to radiation-induced TLS. The intensity of the backward wave in our own experiments put it right in the middle of the intensity-dependent region of Laermans's attenuation data (Fig. 1 of Ref. 5) and our estimated values for α lay within the range of her data (Fig. 2 of Ref. 5). It seems reasonable, therefore, to surmise that we were observing similar defects.

We attempted to identify the detailed mechanism of echo generation by measuring the dependence of the ω-2ω echo power P_E on the acoustic power P_A and the microwave power P_M. The ω-ω echoes were too small in magnitude for meaningful data to be obtained. Typical data are shown in Fig. 3. Regardless of the previous treatment of the samples, and regardless of absolute power levels, the experimental points lay on straight lines of slope approximately equal to unity. A summary of all the results on all the crystals gave

$$P_E \propto P_A^x P_M^y$$

with x and y taking the values

$$x = 0.94 \pm 0.03, \quad y = 1.06 \pm 0.05,$$

for AC cut (transverse);

$$x = 1.01 \pm 0.03, \quad y = 0.98 \pm 0.02,$$

for X cut (longitudinal). These results were unexpected because, as will be explained below, these are the dependences that would be predicted from the intrinsic theory of lattice nonlinearity. In this theory, the free energy of the lattice, V, is expanded in a Taylor series[1] in electric field E and strain S:

$$V = \tfrac{1}{2}cS^2 + \frac{1}{3!}C_{\mathrm{NL}}S^3 - \tfrac{1}{2}\epsilon E^2 - \frac{1}{3!}\chi E^3 - eES - qE^2S + \tfrac{1}{2}fES^2 + \tfrac{1}{2}gE^2S^2 + \frac{1}{3!}hES^3 + \dots \quad (1)$$

The tensor nature of these coefficients will not be considered since our experiments were not designed with sufficient resolution to isolate individual components. Our general conclusions will not be affected, however

TABLE I. Summary of the experiments carried out on five specimens. Uncertainties are estimated to be ± 2 dB for P_{E0} and $\pm 10\%$ for T_2. The quantity P_{E0} is the echo power extrapolated to zero pulse separation.

Crystal	Run	Comment	P_{EO} (dB)	T_2 (10^{-6} s)	Number of reflection echoes
X #1	1 (5/11)	as received	20	80	> 30
	2 (20/1)	face damaged	21	80	17
	3 (26/2)	one month later	24	14	5
	4 (4/3)	one week later	26	13	4
X #2	1 (1/3)	cracked as received	20	28	20
X #3	1 (9/3)	as received	18	29	3
	2 (13/5)	two months later	20	27	10
	3 (14/5)	quenched	28	> 60 (H) 32 (L)	10
	4 (20/5)	quenched again	31	35	10
	5 (23/5)	annealed	18	64	14
AC #1	1 (25/2)	cracked as. received	16	60	8
AC #2	1 (18/5)	as received	24	54	15
	2 (19/5)	quenched	26	> 100 (H) 54 (L)	10
	3 (24/5)	annealed	3	110	> 30
	4 (25/5)	quenched	11	54	10

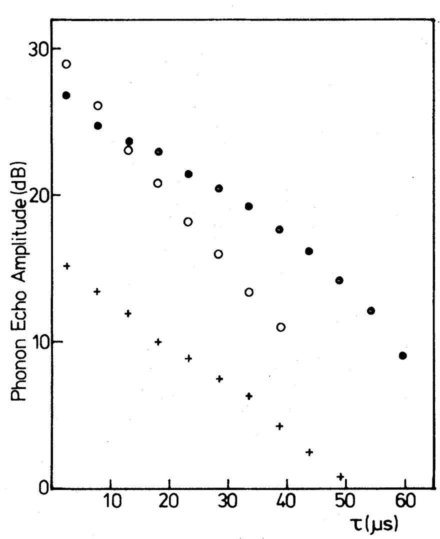

FIG. 2. The magnitude of the phonon echo measured as a function of the separation of the exciting pulses for X No. 3. Key: run 3, quenched (solid circles); run 4, quenched again (open circles); run 5, annealed (plusses).

It can be shown that the expression for the driving stress T_B of the ω-2ω backward-wave echo is given by

$$T_B = (f + 4eq/\epsilon - e^2\chi/\epsilon^2)E_M S_F, \quad (2)$$

where S_F is the strain of the forward-propagating acoustic wave and E_M is the electric field of the

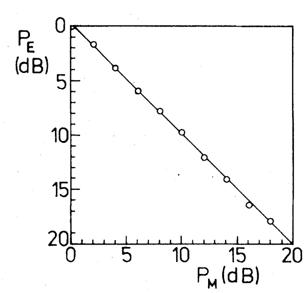

FIG. 3. The dependence of echo power P_E (extrapolated to zero pulse separation) on P_M, the microwave power of the second exciting pulse, for X No. 3, run 5.

second microwave pulse. The first term in (2) represents the direct coupling between the two acoustic strains and the microwave field. The second and third terms arise from the coupling through the electric fields associated with one or both of the acoustic waves. Order-of-magnitude estimates for the various coefficients were obtained from static nonlinear electrostriction data due to Gagnepain and Besson,[7] from impact-loading measurements of third-order piezoelectricity by Graham,[8] and from electro-optic data.[9] We took values for f, q, e, ϵ, and χ of 5 C m^{-2}, 2×10^{-10} F m^{-1}, 0.2 C m^{-2}, 4×10^{-11} F m^{-1}, and 10^{-21} F V^{-1}, respectively. Substituting these values into (2) shows that the first two terms are almost exactly equal, while the third term is two orders of magnitude smaller.

Since the series (1) is an intrinsic physical property of the crystal structure, it has always been assumed that this mechanism for generating echoes does not depend on the defect content of the sample. However, we believe that the large internal strains which accompany defects can give rise to significant enhancement through higher-order terms. If, in the expansion for V, S is written explicitly as the sum of the acoustic stress and the static stress S_0, then the coefficients f, e, q, and ϵ are replaced in first order by $f+\frac{1}{3}hS_0$, $e-\frac{1}{2}fS_0$, $q-\frac{1}{2}gS_0$, and $\epsilon+2qS_0$. The dependence of T_B on S_F and E_M remains unchanged, so that the linear power dependences are maintained—even though the generation depends on strains due to defects. Unfortunately, we do not have values for g and h, but the ratios of the magnitudes of f and e (~25) and of $2q$ and ϵ (~10) suggest that strains between 10^{-1} and 10^{-2} in magnitude would be large enough to cause the echo enhancement observed in our experiments. Attempts to vary the magnitude of the observed echoes by applying external stress to the samples have so far proved unreproducible. We infer therefore that the internal strains are certainly larger than can be produced by external means, $\sim10^{-3}$. It is relevant to note that Gagnepain and Besson themselves observed large variations in electrostriction between samples with varying concentrations of visible defects.

The analysis above is clearly oversimplified since we have ignored both signs and symmetries of the various tensors. In addition, any expansion in terms of infinitesimals is of doubtful validity for strains of so large a magnitude. However, we believe that we have shown convincingly how phonon-echo generation in single crystals can be significantly modified by the presence of structural defects. Although much work remains to be done before a total understanding of the mechanisms is achieved, a clear and immediate implication of our results is that a simple linear power dependence cannot be taken as proof of an intrinsic mechanism of echo generation. Furthermore, great care must be taken to characterize the defect condition for samples for phonon-echo studies if the data are to be regarded as meaningful. We are grateful to N. S. Shiren for useful discussions, and to the Science and Engineering Research Council (U.K.) for supporting the work.

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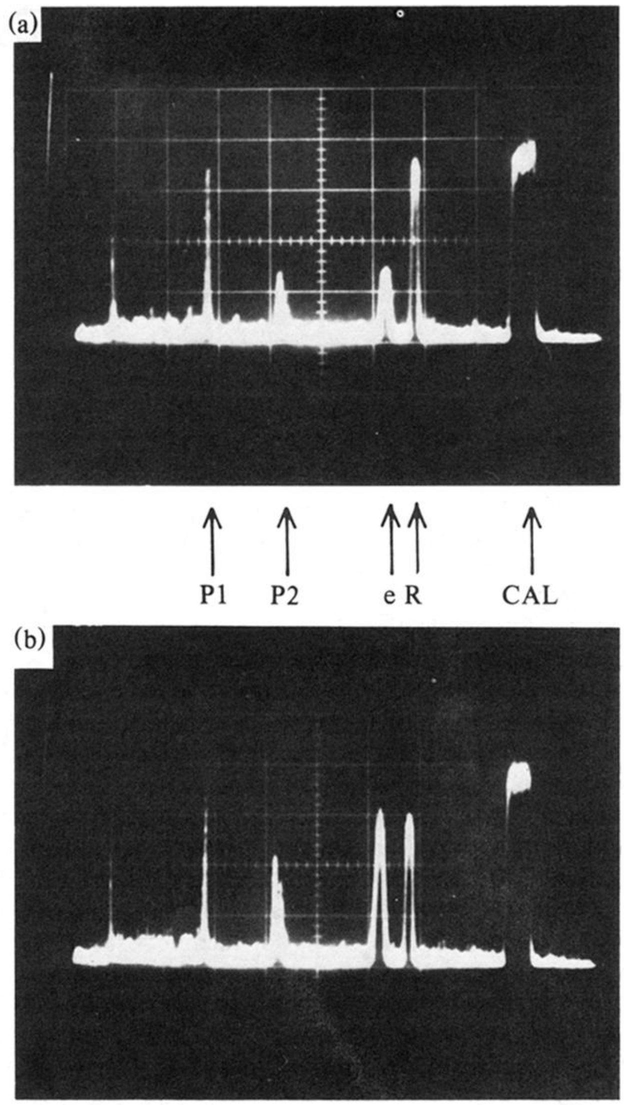

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