Observation of (ω,ω) backward-wave phonon echoes in quartz crystals after neutron irradiation, electrodiffusion, and annealing

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(Received 6 May 1987)

We have studied (ω,ω) backward-wave phonon echoes at 9.3 GHz in quartz crystals which are induced by neutron irradiation, electrodiffusion in vacuum, and heating in vacuum. It is argued that the backward-wave phonon echoes in the electrodiffused and annealed samples are due to impurity atoms present in the quartz crystal and which undergo a migration by this treatment. In the neutron-irradiated samples experimental evidence is found that there are two mechanisms present for the echo generation: two-level systems and impurity atoms, the latter being displaced by the irradiation.

Backward-wave phonon echoes[1] are due to a nonlinear interaction between microwave electric fields and sound waves in solids. The technique of backward-wave echoes can be used to study the hypersonic attenuation in crystals for which the acoustic quality is so bad that no reflection echoes can be detected. Besides this practical application, backward-wave phonon echoes can give information about defects which couple simultaneously to hypersonic waves and to electric fields.

In crystals backward-wave phonon echoes can arise from the intrinsic nonlinearity of the lattice[2] or from impurities.[3] In glasses the amplitude of the backward-wave phonon echo was found[4] to be proportional to the number of OH^- ions, and the generation mechanism was described by a nonlinear resonant mixing process at two-level systems (TLS) associated with the OH^- ions. Backward-wave phonon echoes were also observed in neutron and x-ray-irradiated quartz crystals by Wigmore *et al.*[5] and simultaneously in neutron-irradiated quartz crystals by Vanreyten and Michiels,[6] the latter using them for velocity measurements. Wigmore *et al.*, suggested that the backward-wave phonon echoes (BWE) arise from the TLS and from the aluminum-hole centers.

In the present paper we report measurements of the echo power as a function of incident power in neutron-irradiated quartz before and after annealing to 790 °C. As possible active centers we will discuss the TLS, the aluminum-hole centers, and the OH^- centers. We report also the observation of backward-wave phonon echoes in quartz crystals after electrodiffusion in vacuum and also after heating up to 800 °C. It is argued that these echoes are related to impurity atoms, and the relation with the backward-wave echoes in neutron-irradiated crystals is discussed.

The X-cut natural α-quartz is placed in the high-electric-field region of a reentrant cavity. Pulses of hypersonic waves are excited into the crystal using the surface excitation method[7] at 9.3 GHz. At a time τ after the first pulse, a second microwave pulse is applied to the cavity. The two pulses are obtained from the same continuous wave source. A backward propagating wave is generated due to a nonlinear interaction between the hypersonic wave and the microwave electric field. At time 2τ this backward wave reaches the detecting surface and gives rise to an echo. The width[1] of the backward-wave echo is $\Delta t_1+2\Delta t_2$, with Δt_1 and Δt_2 the pulse width of the first and second pulse. In our experiments we used $\Delta t_1=1$ μs, $\Delta t_2=0.5$ μs, and $\tau=2.8$ μs, both pulses having the same microwave peak power.

(a) Neutron-irradiated quartz. A first crystal was exposed to fast neutrons at Studiecentrum voor Kernenergie (SCK) Mol, Belgium, with a dose of 8.7×10^{19} neutrons per cm^2 ($E>0.1$ MeV). Figure 1 shows the backward-wave echo power P_E as a function of microwave peak power P_i for different temperatures. At 0.9 K and with an incident power of 4 W, we measured the echo power to be -90 dBm. The curve at 0.9 K shows three regimes.

(b) Neutron-irradiated quartz annealed. It was shown[8] that in neutron-irradiated quartz the electric dipole moment associated to the two-level tunneling systems has a magnitude similar to the electric dipole moment associated with intrinsic tunneling centers in pure a-SiO_2. The response of such a defect which couples both to electric fields and acoustical waves can result in the generation of a backward-wave phonon echo.[3,4]

A second defect in neutron-irradiated α-quartz which also couples to electric fields[9] and acoustical waves[10] is the aluminum-hole center[11] ($[AlO_4]^0$ center), in which the hole can tunnel between two equivalent oxygen sites. This $[AlO_4]^0$ center is responsible for the observed smoky color after irradiation. In order to destroy the $[AlO_4]^0$ centers so that in our observations on neutron-irradiated quartz one can make a distinction between the effect of the TLS and of the aluminum-hole centers, one has to anneal[12,13] the sample at 800 °C. After annealing our sample at 790 °C, the smoky color disappeared and we made measurements of the variation of sound velocity with temperature. From these measurements one can determine[14] $C_L=\bar{P}\gamma_L^2/\rho v_L^2$, with $\bar{P}$ the spectral density of the TLS, γ_L the longitudinal deformation potential, v_L the

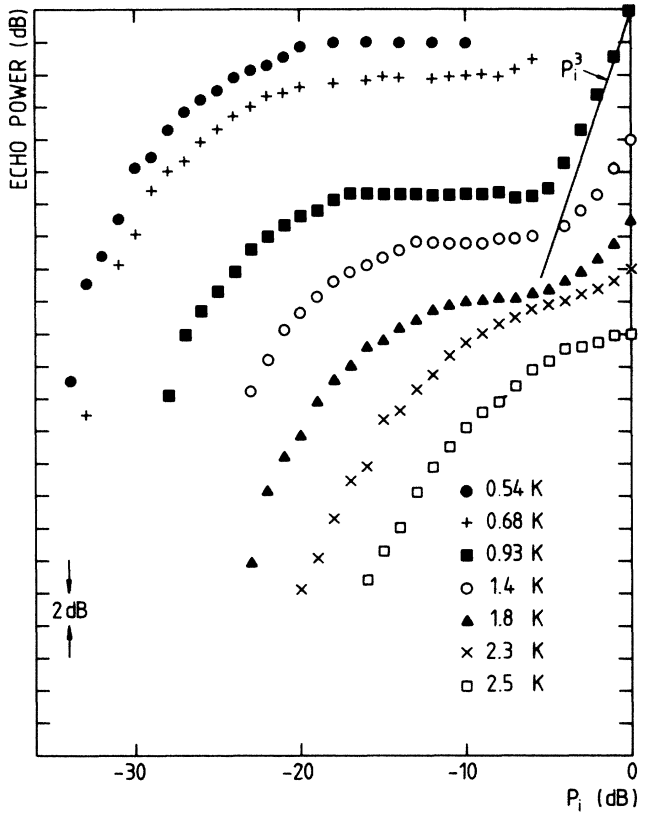

FIG. 1. The backward-wave echo power as a function of the microwave power for different temperatures for the 8.7×10^{19} neutrons per cm^2 irradiated crystal. 0 dB corresponds with a peak power of 4 W. The data for different temperatures are shifted arbitrarily.

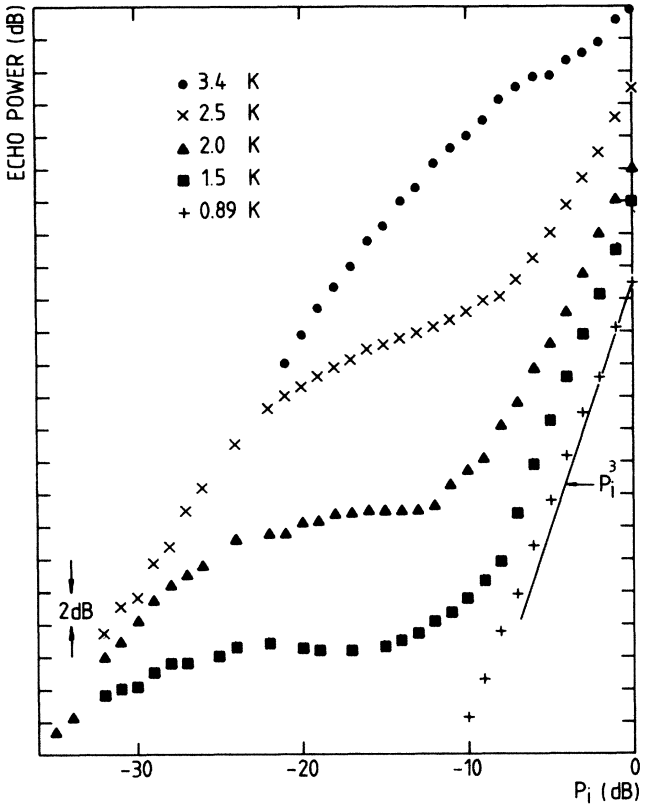

FIG. 2. The backward-wave echo power as a function of microwave power for different temperatures for the 8.7×10^{19} neutrons per cm^2 irradiated but 790 °C annealed crystal. 0 dB corresponds with a peak power of 4 W. The data for different temperatures are shifted arbitrarily.

longitudinal sound velocity, and ρ is the mass density. Before annealing we found $C_L = 158\times10^{-6}$, which is about one half the value of C_L for a-SiO_2.[15] After annealing, C_L decreased by a factor of 2. The backward-wave echo power at 0.9 K (incident power of 4 W) was not decreased by annealing but increased a few dB. As can be seen from Fig. 2, the behavior of the echo power as a function of the incident power is similar as before annealing, although below 1 K we do not observe a plateau. At 1.5 and 2.0 K the three regimes can be seen. This annealing experiment indicates that the aluminum-hole center, although it couples to both electric and elastic fields, cannot be responsible for the backward-wave echo generation mechanism in neutron-irradiated quartz.

Shiren, Arnold, and Kazyaka found[4] that in glasses the amplitude of the backward-wave phonon echo is proportional to the concentration of OH^- ions as measured by the infrared absorption at 2.7 μm. In a-SiO_2 this band is ascribed[16] to the O—H stretching mode of $\equiv$Si—OH. Bates, Hendricks, and Shaffer found[17] that neutron-irradiation of α-quartz also creates this band. Infrared spectra show that before and after annealing this band is also present in our crystals (concentration about 6×10^{18} ions cm^{-3}). Now we can turn to the question if in neutron-irradiated quartz the OH^- ions can also be responsible for the backward-wave phonon echoes.

(c) Quartz, after electrodiffusion. Natural α-quartz crystals contain OH^- groups located at a variety of defect sites. They give rise[18] to infrared-absorption bands in the region of 3200–3600 cm^{-1}. A well-known center is the Al-OH^- defect, which is an OH^- ion adjacent to a substitutional aluminum atom. Also LiOH, NaOH, and H_2O molecules are present as interstitial impurities in the channels of the quartz structure. Interstitial alkali-metal ions Li^+, Na^+, and K^+ are present in a natural quartz crystal as charge compensators and form the Al-Na^+, Al-Li^+ and Al-K^+ centers. The Al-Na^+, Al-K^+, and the Al-OH^- centers give rise to high temperatures ($T > 30$ K) peaks in the dielectric[19] and acoustical[20] loss measurements. In order to find out if, for instance, the Al-OH^- center could be responsible for the generation of the backward-wave phonon echoes, we tried to increase the concentration of Al-OH^- centers by electrodiffusion in vacuum of an as received X-cut quartz crystal. The effects of this electrodiffusion experiment were similar to those reported by Krefft[21] for electrodiffusion in vacuum along the C axis of a quartz crystal. Our crystals were exposed to an electric field of 900 V cm^{-1} along the x axis in vacuum at temperatures of 800 °C and 550 °C. The main effects of this treatment on the measured infrared spectra of our crystals is the decrease of the LiOH and NaOH concentration and the increase of the concentration of the Al-OH^- centers. No evidence for the existence of the 2.7 μm OH^- band was found in these crys-

tals. The reduction of alkali-metal ions, associated with OH^- ions, is due to the fact that Li^+ and Na^+ ions can diffuse under influence of an electric field along the channels parallel[22] to the x axis. After this treatment the crystals were macroscopically damaged so that only small reflection echoes could be observed, but we detected backward-wave phonon echoes of similar magnitude as in neutron-irradiated quartz.

Figure 3 shows for an electrodiffused sample the backward-wave echo power as a function of incident power at different temperatures. In this 800 °C-electrodiffused sample we did not observe a plateau, but the dependence of P_E on P_i becomes weaker as the temperature increases. If one compares these data with the data of the neutron-irradiated sample above -10 dB, a similar path can be seen. A crystal electrodiffused in vacuum at 550 °C shows the same behavior.

Since we did not detect a variation of sound velocity with temperature, nor a temperature dependence of the hypersonic attenuation, we may conclude that there are no TLS present in the electrodiffused samples. In such a case the echo power can be measured as a function of temperature and depends only on the backward-wave generation mechanism. We found that the temperature dependence of the echopower can be described by $P_E \propto T^{-2}$.

(d) Quartz, after annealing. To find out whether the reported results on the samples after electrodiffusion are due to a thermal effect, a sample as received was heated under vacuum to a temperature of 800 °C during a period as long as the duration of the electrodiffusion (56 h). While the untreated quartz crystal showed no backward-wave phonon echoes, we found them again in the annealed sample and also in a sample annealed for only 5 h. The echo power is 10 dB smaller than in the crystals after electrodiffusion but shows the same temperature dependence. From the infrared spectrum we deduced that the heat treatment increases the Al-OH^- concentration in agreement with the observation of Wood.[23] The concentration of these defects was in the annealed sample the same as in the quartz crystal after electrodiffusion but only a factor of 2 higher than in an untreated natural α-quartz crystal which shows no backward-wave phonon echoes. Therefore the backward-wave phonon echoes in the annealed and in the electrodiffused quartz cannot be due to OH^- ions associated with the aluminum centers. They have to be related to the *alkali-metal ions,* since heating produces no defects, but only a migration[23] and subsequent trapping of these impurity ions. The imposed collective migration of the impurity ions in an electrodiffusion experiment can account for the larger backward-wave echo compared with the annealed samples.

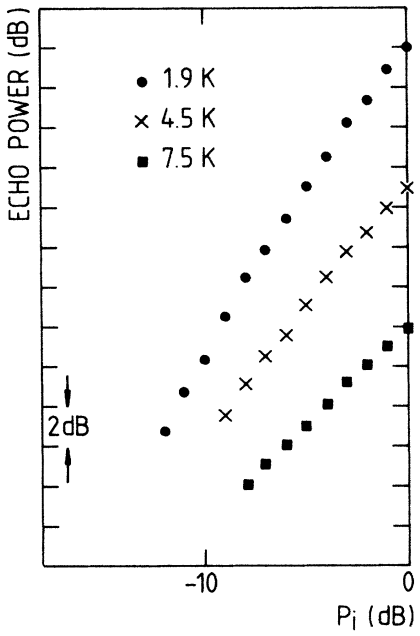

FIG. 3. The backward-wave phonon echo power as a function of incident power for different temperatures for the electrodiffused crystal at 800 °C. 0 dB corresponds with a peak power of 4 W. The data for different temperatures are shifted arbitrarily.

From the measured value of C_L one can calculate that the unsaturated resonant absorption at 9.3 GHz and at 1 K for the 8.7×10^{19} neutrons per cm^2 irradiated quartz sample is 50 dB cm^{-1}. Since we observe at 1 K and at $P_i \simeq -15$ dB an attenuation of only a few dB, it is clear that in our experiments saturation of the TLS occurs. The increase of the backward-wave echo power and the bending off to a plateau points to saturation effects. The low end of the plateau (P_{Pl}) shifts to higher values as the temperature increases and we find $P_{Pl} \propto T^{2.4}$. This temperature dependence is similar as the temperature dependence of the critical acoustical intensity.[24]

Comparing Figs. 1 and 2 we see that at $T \simeq 0.9$ K the plateau value of the echo after annealing is below the noise level of the receiving system, while before annealing the plateau can be clearly observed at this temperature. Since in the resonant mixing process[3] at TLS the echo power is proportional to $\bar{P}^2\gamma_L^4$ (which decreases by a factor of 4 by annealing), we expect that, if the TLS are involved in the generation mechanism, the echo power decreases after annealing, and this is what we observe at low input power. However, at the highest input power ($P_i = 0$ dB) the echo power did not decrease after annealing. Therefore it is likely and we will demonstrate it further on that two different defects are responsible for the observed backward-wave phonon echoes in neutron-irradiated quartz: Firstly, the TLS at low input powers and secondly, at high input powers (where the TLS are saturated) another defect is dominant.

Because the existence of OH^- centers in the samples we cannot exclude the occurrence of TLS associated with OH^-, similar to those found in vitreous silica suprasil I. The critical electromagnetic intensity for saturation of these OH^- associated TLS at 10 GHz is,[25] at 1 K, 1 W cm^{-2}. In our experimental setup the electric field on the spot of the sample is estimated to be 10^4 V m^{-1} at $P_i = 0$ dB, giving an electromagnetic intensity of about 53 W cm^{-2}. Therefore at 1 K the TLS associated with OH^- are electromagnetical saturated for $P_i > -10$ db. When unsaturated TLS are responsible[3] for the generation of backward-wave phonon echoes through a resonant non-

linear mixing process at the TLS, it gives rise to a P_i^3 law for P_E. Because we observe at $P_i > -10$ dB a P_i^3 law, while the intrinsic TLS are acoustical saturated and the possible OH^- associated TLS are electromagnetical saturated, we can conclude that in neutron-irradiated quartz the backward-wave phonon echoes at $P_i > -10$ dB are not due to the resonant nonlinear mixing process at TLS. After all, at high input powers a common origin for the backward-wave generation mechanism in the neutron-irradiated crystal on the one hand, and the electrodiffused and heated crystals on the other hand seems to be acceptable: impurity atoms which migrate upon the influence of the different treatments. Indeed, among various other defects,[17,26,27] neutron-irradiation produces a displacement of the alkali-metal ions, and upon annealing they do not return to their original sites.[19,20]

In crystals the production of backward-wave phonon echoes can be expressed by the wave equation[28] with an effective elastic constant $C_{\text{eff}} = C_0 + C_1 E + C_2 E^2 + \cdots$, where E is the electric field. The amplitude of the (ω,ω) backward-wave phonon echoes is proportional to C_2, while the amplitude of the $(\omega,2\omega)$ echoes (the frequency of the electric field is twice the frequency of the hypersonic wave) is proportional to C_1. For quartz crystals C_2 is too small to make this process responsible for the observed echoes, unless we agree with the suggestion of Fossheim and Holt[28] that an enhancement of the nonlinearity C_2 can be caused by the presence of impurities or defects in a particular configuration. Miyasato *et al.*[29] found an enhancement of the $(\omega,2\omega)$ echoes after fast cooling their quartz crystals to 77 K. They explained their measurements by an enhancement of the intrinsic lattice nonlinearities by internal strains produced by defects. However,this mechanism predicts no temperature dependence of the backward-wave echoes and therefore a similar mechanism as for C_1 can not explain our measurements on the echoes in quartz after electrodiffusion and annealing.

In conclusion, we have observed (ω,ω) echoes in natural quartz crystals, after neutron-irradiation, and for the first time after electrodiffusion at high temperatures in vacuum, and after annealing at 800 °C in vacuum. In the electrodiffused and annealed crystals we suggested that alkali-metal ions which are displaced by the treatment are responsible for the observed echoes. In the neutron-irradiated samples, the input-power dependence of the echo power before and after annealing suggests that two defects are responsible for the observed echoes: the TLS at low input power, and at high input power the alkali-metal ions in a new configuration due to a displacement induced by the irradiation (cf. the electrodiffusion experiment).

We are grateful to the Belgian Interuniversitair Instituut voor Kernwetenschappen (IIKW) for financial support and SCK Mol, Belgium for irradiating the crystals. We also thank Dr. T. Zeegers-Huyskens and M. Graindourze from the Department of Chemistry of the Katholieke Universiteit Leuven for measuring the infrared transmission spectra.

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