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Two-level systems in electron-irradiated quartz

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The longitudinal ultrasonic attenuation in electron-irradiated crystalline quartz (dose of 1.0×10^{20} e/cm^2, $E=2$ MeV) was measured in the temperature range 1.4–300 K, at a frequency of 640 MHz. The data show conclusive evidence for the existence of two-level systems, similar to those in glasses. A relaxation attenuation is observed, giving rise to a T^3 behavior at the lowest temperatures that levels off to a shoulder at about 10 K. The derived density of states is smaller than that in vitreous silica.

At low temperatures amorphous solids exhibit dynamical properties which are unexpectedly different from those in crystals.[1] They can be attributed to the existence of configurational tunneling states,[2] which are successfully described as two-level systems (TLS).[3] The microscopic origin of these TLS is not clear yet. In an attempt to contribute to this study, crystalline solids with defects, such as irradiated crystals, have been investigated. Similar anomalies as in glasses were observed in slightly neutron-irradiated quartz.[4-7] They were explained by the presence of TLS with a density of states which is smaller than in vitreous silica and which increases with neutron dose. The key idea to study defective crystals is that crystalline environments of a defect (possibly extended) which is, or contains the TLS, are easier to study than random networks. In an early stage of our research in irradiated quartz, it was recognized that fast neutrons, because of their mass, induce extended damage regions since they cause displacement cascades. On the other hand, high-energy electrons are not able to cause cascades and as a consequence simpler defects are expected which should be easier to identify. For this reason one of us was involved in low-temperature thermal conductivity studies[8,9] in electron-irradiated quartz. For temperatures below 1 K a significant radiation-induced thermal resistivity was found and it was shown that this could be explained by scattering of phonons at TLS similar to those in neutron-irradiated quartz and in glasses. Until now this is the only published evidence for the presence of TLS in electron-irradiated quartz. As a consequence it was not generally accepted that electrons can induce TLS. Here we present conclusive evidence for its "glassy" behavior from ultrasonic attenuation studies carried out in a temperature range 1.4–300 K.

A single crystal of natural Brazilian quartz, x cut and of high purity was electron irradiated up to a dose of 1.0×10^{20} e/cm^2 ($E=2$ MeV). Neutron activation analysis yielded as impurity in μg/g:

Al 12, Cr 9, Fe 65, Mn 0.3, Ti 17 ,
Co 0.4, Cu 22, K 60, Na 7.8, V 0.8 .

The electron irradiation was done in a Van de Graaf generator with a flux of 2.6 A/cm^2. The longitudinal ultrasonic attenuation of this sample was measured in the temperature range 1.4–300 K at a frequency of 640 MHz, using the pulse echo technique. The results are plotted in Fig. 1 on a log-log scale. In Fig. 2 the results for a neutron-irradiated sample of the same origin (N$_2$, dose: 1.0×10^{18} n/cm^2, $E\gtrsim0.3$ MeV), are given for comparison. Also data for unirradiated quartz of the same origin are shown. For each sample, a temperature-independent residual attenuation α_0, attributed to geometrical factors was subtracted from the data. Indeed, the ultrasonic attenuation levels off at low temperatures and for α_0 a corresponding value is taken.

At the lowest temperatures the electron irradiation

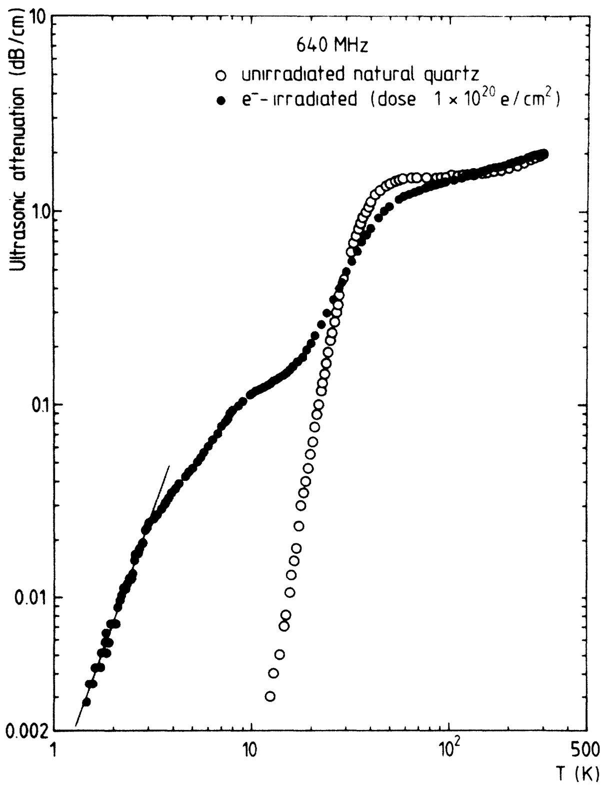

FIG. 1. Ultrasonic attenuation as a function of temperature for $f=640$ MHz. ●, electron-irradiated quartz; ○, unirradiated quartz.

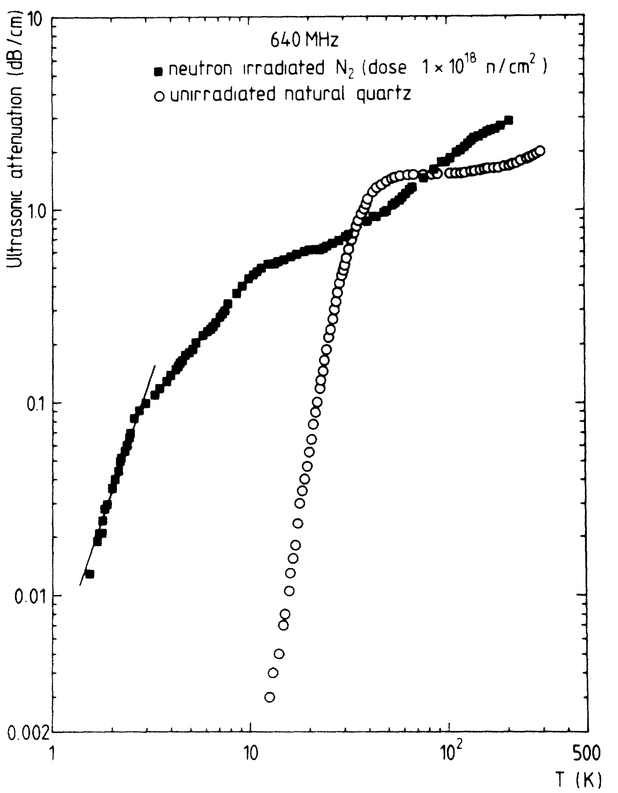

FIG. 2. Ultrasonic attenuation as a function of temperature for f =640 MHz. ■, neutron-irradiated quartz N_2; ○, unirradiated quartz.

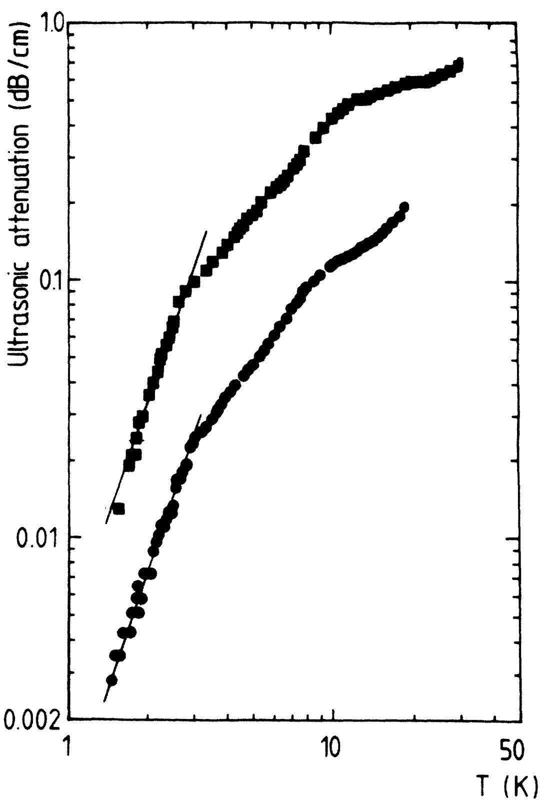

FIG. 3. Low-temperature ultrasonic attenuation for f =640 MHz. ●, electron-irradiated quartz; ■, neutron-irradiated quartz N_2.

causes a remarkable increase of the ultrasonic attenuation compared to the unirradiated crystal. In addition the attenuation is temperature dependent, whereas in the unirradiated sample no temperature dependence was observed in this temperature range. The similarity with the neutron-irradiated sample is striking (see Fig. 3). The temperature dependence can be described by a T^3 law. This behavior is typical for glasses, where it is attributed to the interaction of the ultrasonic phonons with TLS. According to the tunneling model, a high-energy ultrasonic wave changes the energy splittings of the asymmetric double-well potentials of the TLS. Their occupation numbers are brought out of thermal equilibrium. A return to the equilibrium state is accomplished by energy transfer to the thermal phonons. This effect gives rise to a relaxation absorption, leading to a T^3 attenuation at the lowest temperatures where $\omega\tau_m \gg 1$, with τ_m the smallest relaxation time of the TLS.

Another observation that confirms the existence of the TLS in electron-irradiated quartz is the appearance of a shoulder at about 10 K. A similar behavior was found in vitreous silica[3] and in neutron-irradiated quartz (see Fig. 2) for comparable frequencies. It is an effect, which in the tunneling model is attributed to the $\omega\tau_m \ll 1$ regime of the relaxation attenuation and for which a T^0 attenuation is predicted. Only a shoulder is seen and not an extended T^0 range because other attenuation processes become dominant in this temperature range. In the case of our data in electron-irradiated quartz it is the anharmonic three-phonon interaction, which above 10 K causes a strong temperature-dependent attenuation (Akhiezer regime)[10] which masks the T^0 regime of the TLS. Between the T^3 behavior and the shoulder at about 10 K, a transition region is observed, which corresponds to the regime $\omega\tau_m \cong 1$. Also in this region there is a striking similarity with the neutron-irradiated quartz (see Fig. 3). In addition, also in vitreous silica, analogous behavior is observed.[11] From all these similarities, we believe that this low-temperature study gives conclusive evidence for the existence of two-level systems in electron-irradiated quartz.

For the highest temperatures, above 100 K, the electron-irradiated sample and the virgin sample show a behavior which is qualitatively similar: a slow increase with increasing temperature. Quantitatively, the attenuation differs by an approximately constant value. Apart from this value, the attenuation in the electron-irradiated sample, therefore can be described by the same process as in the unirradiated sample, e.g., the $\omega\tau_{\mathrm{ph}} \ll 1$ regime of the anharmonic three-phonon interaction.[10] (τ_{ph} is the phonon-phonon relaxation time.) The constant additional attenuation induced by the electron irradiation corrsponds to the attenuation at the 10-K shoulder which is discussed in the previous paragraph. This would indicate that the $\omega\tau_m \ll 1$ regime of the TLS can be observed up to a temperature of 300 K. As will be discussed further on, the presence of defects can influence the three-phonon interaction. However, this is known to occur mainly in the temperature range below the one we consider here. Therefore the additional irradiation induced attenuation above 100 K is attributed to the TLS.

Now we turn to the intermediate temperature range around 50 K. This region corresponds to the leveling off of the strongly temperature-dependent attenuation due to the anharmonic three-phonon process, when the condition $\omega\tau_{\rm ph}=1$ is approached. As can be seen in Fig. 1, the attenuation is slightly reduced by irradiation. This is a fairly well-known effect and is attributed to the presence of radiation-induced defects, which cause a decrease of relaxation time $\tau_{\rm ph}$.[12] This behavior is similar to that in our neutron-irradiated sample (see Fig. 2) and was also observed before in neutron-irradiated quartz.[13] It can only be observed for low irradiation doses; higher doses give rise to higher TLS density of states and therefore mask this effect.[14]

From the low-temperature data an estimate can be made for some typical parameters of the TLS, used in the tunneling model. According to this model, the longitudinal relaxation absorption α for the low-temperature T^3 behavior (regime $\omega\tau_m \gg 1$) is given by[15]

$$\alpha=\frac{\pi^3 k^3 T^3 \bar{P}\gamma_l^2}{24\rho^2\hbar^4 v_l^3}\left(\frac{\gamma_l^2}{v_l^5}+\frac{2\gamma_t^2}{v_t^5}\right) . \tag{1}$$

The parameters γ_l and γ_t, respectively, represent the coupling of the longitudinal and transverse thermal phonons with the TLS. The term $2\gamma_t^2/v_t^5$ in this expression is based on the assumption that a mean value for both quantities may be used. Making use of the expression $\gamma_l^2=2\gamma_t^2$, we can deduce $\bar{P}\gamma_l^4$ from (1). Taking $v_l=5700$ m/s and $v_t=4400$ m/s, we find

$$\bar{P}\gamma_l^4=1.27\times10^{-18}\,{\rm g^3cm^3/s^6} . \tag{2}$$

On the other hand, $\bar{P}\gamma_l^2$ can be determined from the T^0 behavior in the regime $\omega\tau_m \ll 1$. For this regime the tunneling model predicts an attenuation:[15]

$$\alpha=\frac{\pi\omega\bar{P}\gamma_l^2}{2\rho v_l^3} . \tag{3}$$

As mentioned before, a plateau is not really measured. We only observed a shoulder at about 10 K, because of the strongly temperature-dependent anharmonic phonon-phonon interaction. For this numerical calculation, we have assumed that this process still plays a minor role at 10 K. Hence the measured attenuation at the shoulder is dominated by the plateau regime given by Eq. (3). This assumption is based on the measurements performed on the unirradiated crystal (see Fig. 1), where a negligible attenuation from the phonon-phonon interaction at 10 K is clearly observed. From Eq. (3) a value for $\bar{P}\gamma_l^2$ is obtained:

$$\bar{P}\gamma_l^2=2.14\times10^{6}\,{\rm erg/cm^3} . \tag{4}$$

From Eqs. (2) and (4) values $\gamma_l=0.48$ eV and $\gamma_t=0.34$ eV are deduced. They are smaller than the coupling parameters found in vitreous silica: $\gamma_l=1.1$ eV and $\gamma_t=0.6$ eV, if we use a similar method of calculation. Also in neutron-irradiated quartz we had to explain our ultrasonic attenuation data with values for γ_l and γ_t that are smaller than in vitreous silica,[16] although the difference is less. We note that also in amorphous solids other than vitreous silica, values for γ_l and γ_t smaller by a similar fraction, have been put forward.[17] From (2) and (4) we are able to estimate the density of states of TLS: $\bar{P}=3.6\times10^{30}$ ${\rm cm^{-3}erg^{-1}}$. This is 5% of the number of TLS taking part in the attenuation of vitreous silica.

Concerning the damage induced by MeV electrons in quartz, very few studies are available. Regions of extensive damage such as the 20-Å defective clusters in neutron-irradiated quartz are certainly not present, as is known from diffuse x-ray scattering studies made on one of our samples.[18] Because of their small mass, electrons, as opposed to fast neutrons, cannot cause displacement cascades. The primary knock-on, however, can give rise to a point defect. ESR studies on one of our samples, for instance, show the presence of the E' center,[19] which is mostly known from ESR studies on neutron-irradiated quartz. It is thought to be an $\rm O^-$ vacancy with the remaining electron localized on one of the silicon atoms.[20] An interesting observation in our ESR data on electron-irradiated quartz is that the E' line shows a broadening which is also seen in neutron-irradiated quartz. This could be an indication for more disorder than just a point defect. It might be caused by so-called radiolysis.[21] More ESR work is in progress and we hope that this will be an appropriate tool to probe the local environment of the defects. However, at this stage it is already clear that the TLS in electron-irradiated quartz do not necessarily have to be related to large damage regions.

In summary, the ultrasonic attenuation has been measured in quartz irradiated with electrons up to a dose of 1.0×10^{20} $e/{\rm cm^2}$. The data give conclusive evidence for the presence of two-level systems in electron-irradiated quartz. At the lowest temperatures a T^3 ultrasonic attenuation was observed, which is typical for an attenuation due to TLS. Also, the presence of a shoulder at about 10 K can be attributed to TLS. For the coupling parameters and the density of states of TLS we obtained $\gamma_l=0.48$ eV, $\gamma_t=0.34$ eV, and $\bar{P}=3.6\times10^{30}\,{\rm cm^{-3}erg^{-1}}=5\%\ \bar{P}_{\rm vitr.\,sil.}$. In electron-irradiated quartz, TLS seem to couple less to phonons than in vitreous silica. This phenomenon, although less pronounced, was also found in neutron-irradiated quartz. It might be closely related to the induced damage. Although complete knowledge of electron-induced damage is still lacking, it is clear that TLS in electron-irradiated quartz cannot be related to amorphous clusters.

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