Influence of heat treatment on the tunneling states in neutron-irradiated quartz

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We report the results of a systematic study of the influence of heat treatment on the tunneling states (TS) in neutron-irradiated quartz. Measurements of the ultrasonic attenuation and velocity change are carried out before and after heat treatment, as a function of temperature (0.3–300 K) and in the ultrasonic frequency range (50–650 MHz), on well-characterized specimens. Two doses have been studied, irradiated, and heat treated under similar conditions. One dose is lying well below the so-called threshold dose, the other is situated near the threshold. From numerical fits of the data with the tunneling model, the density of states P and the coupling parameter γ_l were determined independently. This allows us to investigate the influence of the heat treatments on the number and nature of the TS. Attention is paid to both the influence of the annealing temperature and the length of the heat treatment. All samples still show the typical TS behavior after heat treatment, but the density of states is drastically reduced. Regarding the coupling, the two doses show a different behavior: while there is no influence on the coupling for the higher dose, a significant decrease in γ_l is observed for the lowest dose. This decrease can be interpreted in terms of changes in the tunneling entity itself and is in agreement with the changes in the distribution of the TS. [S0163-1829(96)06618-0]

I. INTRODUCTION

In recent years, it has been well established that the low-temperature properties[1] of amorphous solids are successfully described by the existence of low-energy tunneling excitations.[2] These so-called tunneling states (TS) turned out to have a wide distribution of energies and relaxation times, their microscopic origin, however, is still unclear. In an attempt to contribute to this study, crystalline solids with defects have been investigated, allowing a comparison between the type of disorder and the TS. In particular neutron-irradiated quartz turned out to be very attractive as a model of the glassy state, since varying the neutron dose allows continuous structural variations from the perfectly ordered crystal to the amorphous network disorder. In our laboratory, an extensive study of the TS in irradiated quartz is being carried out. The ultrasonic attenuation and velocity change have been measured on well-characterized samples, irradiated under similar conditions, in the same reactor. These investigations clearly evidenced that neutron- and electron-irradiated quartz show ''glassy anomalies,'' which can be explained by the presence of tunneling states, similar in nature to those in vitreous silica but with a lower density of states.[3–5] In the dose range studied in our laboratory, the density of states was found to increase with increasing dose. The coupling parameter appeared to be somewhat smaller than in vitreous silica, with a tendency to increase slightly with the dose. The measurements made also clear that the TS do not only reside in the ''amorphous''[6] regions: an important part of the TS in irradiated quartz has to be attributed to the remaining ''crystalline'' part of the samples.[7] In order to obtain more information about the origin of these ''crystalline'' TS, we carried out recently ultrasonic measurements in neutron-irradiated z-cut quartz (whereas all previous measurements involved only x-cut specimens).[8] This study revealed a remarkable anisotropy in the behavior of the TS, which has to be attributed to the tunneling mechanism itself. These results gave evidence for the α_1-α_2 Dauphiné twins as microscopic origin of the ''crystalline'' TS, leading to a description of the tunneling mechanism as a rotation of coupled SiO_4 tetrahedra.

This paper deals with the results of a systematic study of the TS in neutron-irradiated quartz after heat treatment. It is known that, depending on the dose, neutron-irradiated quartz evolves after annealing to α-quartz or to a-SiO_2. According to Mayer and Lecomte,[9] the threshold separating these two regimes is situated around a dose of approximately 6×10^{19} n/cm^2. However, this dose is not well defined and should rather be seen as a ''threshold region'' instead of a sharply defined threshold dose. Figure 1 represents the evolution of neutron-irradiated quartz after heat treatment: quartz irradiated up to a dose below the shaded threshold region evolves after annealing to α-quartz. The mass density of these specimens will thus increase after heat treatment. For doses above the threshold, the mass density of the irradiated samples decreases after annealing, the specimens evolve to a-SiO_2. Gardner and Anderson[10] carried out measurements of the thermal conductivity and specific heat on neutron-irradiated quartz and concluded that the TS excitations remain unchanged after heat treatment. However, whereas thermal experiments involve averages over energies, acoustic measurements are monochromatic and reveal information about the TS in a specific spectral region. Therefore, ultrasonic measurements can give additional information about the behavior of the TS after heat treatment.

The experiments discussed in this work are carried out for two doses: N4 (1.2×10^{19} n/cm^2), lying well below the threshold, and N6 (4.7×10^{19} n/cm^2), situated near or in the threshold region (see Fig. 1). The samples have been heat-treated for various annealing times and at several temperatures. After each heat treatment, measurements of the ultrasonic absorption and velocity change are performed as a

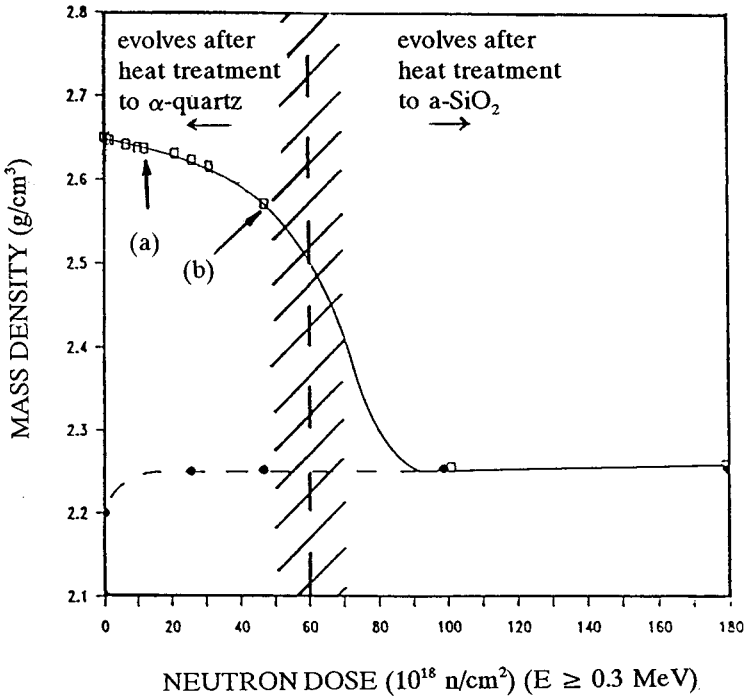

FIG. 1. Density of neutron-irradiated quartz for doses below and above the ''threshold dose'' of 6×10^{19} n/cm^2 ($E\geqslant0.3$ MeV). (a)=our dose N4, (b)=our dose N6.

function of temperature, at different frequencies. This provides us with an extensive series of data, which are quantitatively analyzed with the tunneling model, and allows a study of the influence of heat treatment on the TS parameters as a function of the dose, the annealing temperature and the annealing time.

II. THEORETICAL CONSIDERATIONS

In the tunneling model[2] the TS arise from atoms or groups of atoms which have two possible equilibrium positions of nearly equal energy. They are presented as particles (with total mass m) moving in an asymmetric double well potential, with distance d between the two minima and a barrier V separating the wells (Fig. 2). The energy difference between the eigenstates is given by $E=\sqrt{\Delta^2+\Delta_0^2}$ where Δ is the asymmetry of the double well. Δ_0 is the tunnel splitting, given by $\Delta_0=\hbar\Omega\exp(-\lambda)$ and λ describes the overlap of the wave functions $[\lambda=d(2mV/\hbar^2)^{1/2}]$. One of the basic assumptions of the tunneling model is that Δ and λ are independent of each other and are uniformly distributed:

$$P(\Delta,\lambda)d\Delta d\lambda=\overline{P}d\Delta d\lambda \tag{1}$$

with $\overline{P}$ a constant, the density of states of the TS. This equation can also be written in terms of E and Δ_0:

$$P(E,\Delta_0)=\overline{P}\,\frac{E}{\Delta_0(E^2-\Delta_0^2)^{1/2}}. \tag{2}$$

The effect of the TS on the low-temperature ultrasonic properties arises from two different mechanisms. First, the sound wave will be resonantly absorbed by those TS having an energy splitting E corresponding to the phonon energy ($E=\hbar\omega$). Because of the wide distribution of energy splittings, this process occurs at all frequencies and leads to a frequency-independent but temperature-dependent change in the velocity of sound, given by[11]

$$\frac{\nu(T)-\nu(T_0)}{\nu(T_0)}=C\,\ln\frac{T}{T_0}=\frac{\overline{P}\gamma_l^2}{\rho\nu_l^2}\ln\frac{T}{T_0} \tag{3}$$

provided that $\hbar\omega\ll kT$. T_0 is an arbitrary reference temperature and γ_l represents the coupling of the TS with the longitudinal phonons. For our absorption measurements, this process need not be considered, since its contribution in this high-energy experiment is negligible.

The second process is the relaxational process. According to the tunneling model, a strain wave changes the energy splittings of the asymmetric double well potentials of the TS. In this way, the thermal equilibrium distribution of the TS is disturbed. In dielectric amorphous materials, the return to the equilibrium state occurs via interaction with the thermal phonons. At low temperatures, the most dominant process is the one-phonon process, giving rise to a relaxation rate,[1]

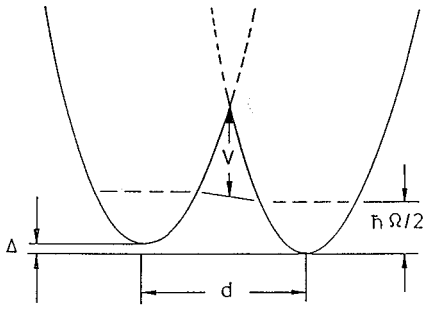

FIG. 2. Formal presentation of the tunneling states according to the tunneling model; V=barrier height, Δ=asymmetry, and d=distance between the minima.

$$\tau^{-1}=K_3\left(\frac{\Delta_0}{E}\right)^2\left(\frac{E}{2k}\right)^3\coth\left(\frac{E}{2kT}\right)$$

with

$$K_3=\frac{4k^3}{\rho\pi\hbar^4}\left(\frac{\gamma_l^2}{\nu_l^5}+\frac{2\gamma_t^2}{\nu_t^5}\right), \tag{4}$$

where γ_l and γ_t represent the coupling of the TS with, respectively, the longitudinal and transverse phonons.

The distribution given by Eq. (2) has direct consequences for the relaxation times of the TS. Since the relaxation rate τ^{-1} is proportional to $(\Delta_0/E)^2$ [see Eq. (4)], a given energy E implies a distribution of τ^{-1}:[12]

$$P(E,\tau^{-1})dE\ d\tau^{-1}=\frac{\overline{P}}{2}\frac{\tau}{[1-\tau_m(E)/\tau]^{1/2}} \tag{5}$$

with τ_m the relaxation time for the fastest relaxing TS (those for which $\Delta_0=E$). Taking into account the distribution of the relaxation times, the relaxational attenuation can be written as[13]

$$l_{\rm rel}^{-1}=\frac{\gamma_l^2}{\rho\nu_l^3kT}\int_{E_{\min}}^{E_{\max}}dE\int_{\nu_{\max}}^{1}\frac{\omega^2\tau}{1+\omega^2\tau^2}\frac{\overline{P}}{u(1-u^2)^{1/2}}\left(\frac{\Delta}{E}\right)^2\times\operatorname{sech}^2(E/2kT)du \tag{6}$$

with $u=\Delta_0/E=(\tau_m/\tau)^{1/2}$. Note that $l_{\rm rel}^{-1}$ is proportional to $\omega^2\tau/(1+\omega^2\tau^2)$, which means that the most important contribution comes from those TS with $\omega\tau=1$.

The expression for the variation of the sound velocity due to the relaxational process is given by[13]

$$\frac{\nu(T)-\nu(T_0)}{\nu(T_0)}=-\frac{\overline{P}\gamma_l^2}{\rho\nu_l^2}\int_{E_{\min}}^{E_{\max}}\frac{1}{2kT}\operatorname{sech}^2(E/2kT)dE\times\int_{\nu_{\min}}^{1}\frac{u^3(1-u^2)^{1/2}}{u^4+(\omega\tau_m)^2}du. \tag{7}$$

Analytic solutions can be found for the limiting cases $\omega\tau_m\gg1$ and $\omega\tau_m\ll1$ and are briefly discussed here. For the low temperatures, the condition $\omega\tau_m\gg1$ is satisfied. In this case, the relaxational attenuation is frequency independent, showing a T^3 behavior:[13]

$$l_{\rm rel}^{-1}=\frac{\pi^3k^3\overline{P}\gamma_l^2}{24\rho^2\hbar^4\nu_l^3}\left(\frac{\gamma_l^2}{\nu_l^5}+\frac{2\gamma_t^2}{\nu_t^5}\right)T^3. \tag{8}$$

In this regime, the relaxation process gives a negligible contribution to the velocity change.[12] For the $\omega\tau_m\ll1$ regime (higher temperatures), the ultrasonic attenuation is temperature independent:[13]

$$l_{\rm rel}^{-1}=\frac{\pi\omega}{2\nu_l}C=\frac{\pi\omega\overline{P}\gamma_l^2}{2\rho\nu_l^2}. \tag{9}$$

This is the so-called plateau in the attenuation, which varies linearly with the frequency. It is a direct consequence of the specific distribution of relaxation times. The variation of the velocity of sound depends logarithmically on temperature in this regime and is frequency independent:[12]

$$\frac{\nu(T)-\nu(T_0)}{\nu(T_0)}=-\frac{3}{2}C\ln\frac{T}{T_0}=-\frac{3}{2}\frac{\overline{P}\gamma_l^2}{\rho\nu_l^2}\ln\frac{T}{T_0}. \tag{10}$$

The expressions given so far are valid provided that the TS relax via absorption or emission of a single thermal phonon.

TABLE I. Ultrasonic attenuation and velocity measurements carried out after heat treatment for the dose N4 (1.2×10^{19} n/cm^2, K2Ni) and for the dose N6 (4.7×10^{19} n/cm^2, K4Ni). For N4 all the measurements are carried out using a cavity. For N6, using $LiNbO_3$ transducers.

Sample	Heat treatment	Density (g/cm^3)	Frequency (MHz)
K2N3	a	2.636±0.002	648[b,c]
	1 h, 300[a] & 400 °C[a]		648[b]
	1 h, 530 °C[a]		648[b,c]
	1 h, 590 °C[a]		648[b,c]
	1 h, 700 °C		648[b,c]
	2 h, & 3 h, 700 °C		648[b]
	14 h, 700 °C	2.650±0.002	648[b]
K2N2	0 min, 840 °C	2.650±0.002	648[b]
K2N1	15 min, 840 °C	2.650±0.003	648,[b] 400[b]
K4N2		2.559±0.002	50,[b] 340[b,c]
	15 min, 840 °C	2.591±0.003	75,[b] 310[b,c]
	1 h, 840 °C	2.592±0.003	84,[b] 305,[b] 310[c]
K4N4	1 h, 700 °C	2.596±0.002	80,[b] 210,[b] 305[b,c]
	2 h, 700 °C	2.590±0.007	80,[b] 340[b]
	17 h, 700 °C	2.593±0.003	80,[b] 310,[b] 305[b,c]

[a]These data are part of the Ph.D. thesis of A. Vanelstraete (K. U. Leuven, 1988, unpublished).
[b]Attenuation measurements.
[c]Velocity measurements.

At higher temperatures, above a few Kelvin, the Raman processes need to be taken into account.[13] A modified relaxation time τ has to be introduced: $\tau^{-1}=\tau_d^{-1}+\tau_r^{-1}$ in which τ_d is the relaxation time for the one-phonon processes and τ_r the relaxation time for the Raman process. This additional process causes a stronger temperature dependence in the transition region from the $\omega\tau_m \gg 1$ to the $\omega\tau_m \ll 1$ regime.

III. EXPERIMENTAL DETAILS AND SAMPLE CHARACTERIZATION

Five synthetic quartz samples, x cut and of high purity (impurity content is given in Ref. 4) were shaped into cylindrical rods with 3 mm diameter and 8 mm length. The end faces were polished optically flat and parallel for ultrasonic studies. All samples were irradiated with fast neutrons ($E \geqslant 0.3$ MeV) in the reactor at the Studiecentrum voor Kernenergie (SCK, Mol, Belgium). Three of these samples (called K2N1, K2N2, and K2N3) were simultaneously exposed to a dose of 1.2×10^{19} n/cm^2 (further denoted as N4), the other (K4N2 and K4N4) were irradiated under the same conditions and during the same reactor cycle, up to a dose of 4.7×10^{19} n/cm^2 (labeled N6). Since the mass density is known to be an unambiguous parameter for the induced damage, accurate mass density measurements were carried out after the irradiations. This allows reliable comparisons with other samples, irradiated in different reactors. Each sample was then subjected to heat treatment, covering an annealing range from 300 to 840 °C, for times varying between 0 min (immediate cooling) and 17 h. Before and after these thermal treatments, ultrasonic measurements have been carried out as a function of temperature. Table I gives a summary of the different heat treatments and the experiments discussed in this paper. The mass density of the samples, measured before and after most of the heat treatments, is also given in the table.

Measurements on unirradiated quartz have been extensively discussed before (see for instance Ref. 4) and are therefore not reported in this paper. The measurements are carried out using a standard pulse-echo technique for rf transmitting and receiving. Accurate $\Delta v/v$ measurements were possible with a modified pulse-interference technique.[14] The longitudinal waves in the samples K2N1, K2N2, and K2N3 were generated by surface wave excitation. For measurements on the higher irradiated specimens K4N2 and K4N4, a $LiNbO_3$ transducer was attached to the sample for converting the electromagnetic signal into an elastic wave, since the irradiation damage deteriorated the efficiency of the surface wave excitation in these samples. At the same time, this technique allows measurements at lower frequencies, down to 50 MHz. Measurements at these frequencies were not possible using surface excitation because the length of the cavity becomes unpractically long for frequencies below 200 MHz. The transducer is bonded to the sample on one of the parallel faces. Amongst the various materials used as bonding agent, Nonaq stopcock grease was found to give the best results for our experiments.

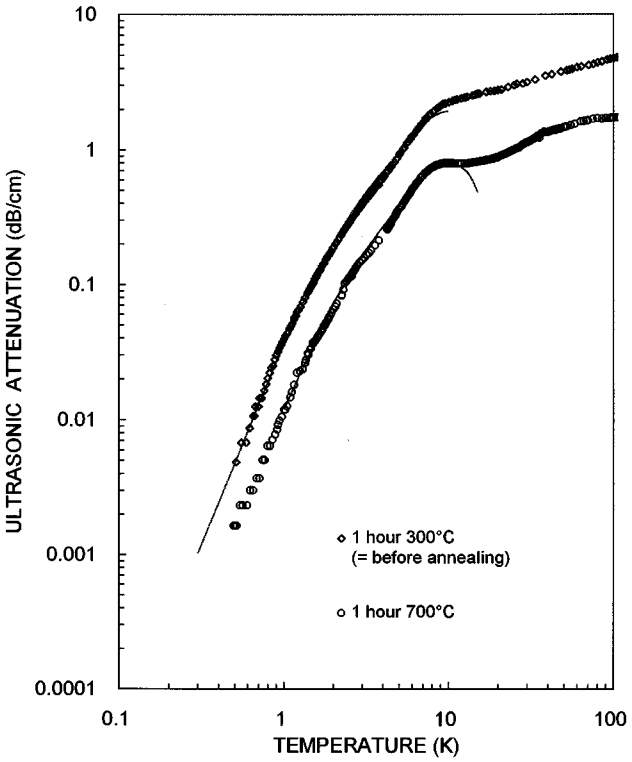

FIG. 3. Ultrasonic attenuation measurements as a function of temperature for neutron-irradiated quartz N4 (dose 1.2×10^{19} n/cm^2), before (top curve) and after heat treatment for 1 h at 300 °C (top curve) and 700 °C (lower curve). Frequency: 648 MHz. — : fitcurve.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Ultrasonic attenuation and velocity measurements after heat treatment for a dose of 1.2×10^{19} n/cm^2

In this section, we will discuss ultrasonic measurements carried out after heat treatment of the samples K2N1, K2N2, and K2N3, all irradiated with a dose of 1.2×10^{19} n/cm^2. Three parts can here be distinguished: first, we discuss experiments carried out as a function of the temperature of the heat treatment, covering an annealing range from 300 to 700 °C, a second part involves measurements after heat treatment at 840 °C; the last part of this section concerns measurements after heat treatment at 700 °C, as a function of the annealing time.

1. The influence of heat treatments at 300 to 700 °C

The attenuation as a function of temperature in K2N3, after heat treatment for 1 h at 300, 400, 530, 590, and 700 °C has been measured. Figure 3 gives the results for 300 and 700 °C. The results for 400, 530, and 590 °C (not shown in the figure) are similar and the attenuation decreases with increasing annealing temperature. All measurements are carried out at a frequency of 648 MHz. The attenuation before heat treatment and after 1 h at 300 °C are identical, therefore only one of them is shown. All curves show a similar qualitative behavior: at the lowest temperatures, the typical T^3 behavior for the regime $\omega\tau_m \gg 1$ of the relaxation absorption

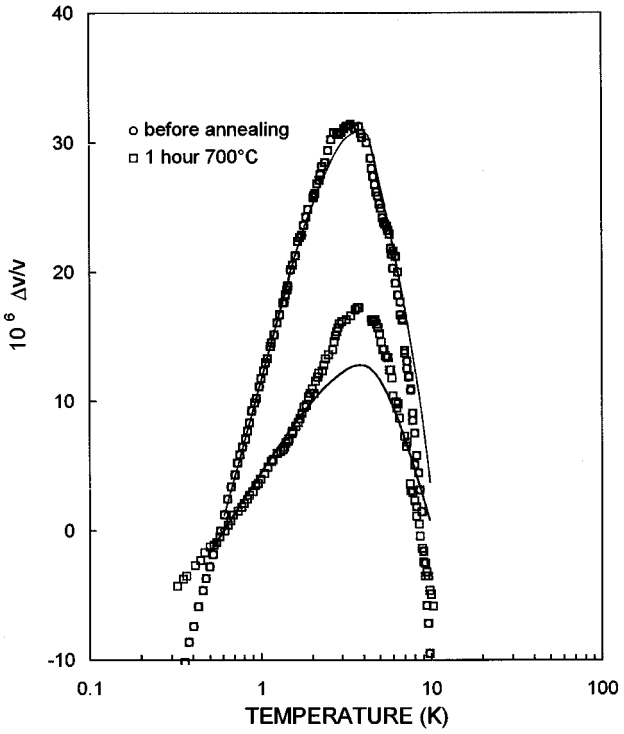

FIG. 4. Ultrasonic velocity change measurements in neutron-irradiated quartz N4 (dose 1.2×10^{19} n/cm^2), before (upper curve) and after annealing for 1 h at 700 °C (lower curve). Frequency: 648 MHz. — : fitcurve.

is observed, which gradually levels off above 1.5 K to a shoulder at about 10 K. This shoulder corresponds to the plateau predicted by the tunneling model, but an extended T^0 range is masked by other processes (such as anharmonic three-phonon processes and thermal relaxation), that become dominant in this temperature range. Heat treatment below 530 °C appears to have no effect on the attenuation, from 1 h at 530 °C on, however, the absorption starts to decrease with increasing annealing. After heat treatment at 700 °C, the value of the attenuation at the plateau is reduced to about half the original value, but the shape of the curve remains unchanged. This indicates that the heat treatment mainly affects the density of states P of the tunneling states.

The velocity change $\Delta v/v=[v(T)-v(T_0)]/v(T_0)$ as a function of temperature, has been measured before and after annealing at 530, 590, and 700 °C. The measurements were carried out at 648 MHz; as reference temperature, $T_0=0.58$ K is taken for all curves. The results are shown in Fig. 4 for an annealing temperature of 700 °C and for the as-irradiated sample. The data for 530 and 590 °C (not shown in the figure) are situated between. All the data show a similar qualitative behavior: at the lowest temperatures, the velocity change increases logarithmically with increasing temperature, which is the result of the resonant interaction between the TS and the phonons. The maximum at about 4 K and the observed velocity decrease at higher temperatures correspond to the region where the relaxation process becomes important. Although the qualitative behavior of all curves is similar, the velocity change decreases with heat treatment. This clearly follows from the slope of the logarithmic increase, which becomes smaller with increasing annealing temperature: after 1 h at 700 °C, $\Delta v/v$ between 0.6 and 1 K is only 50% of the change before heat treatment. These results are consistent with the attenuation measurements and indicate that the density of states P of the TS significantly changes after annealing. Since the temperature of the maximum in $\Delta v/v$, $T_{\max}$ is about the same for all the curves, the coupling parameter γ_l between the TS and the phonons will be of the same order of magnitude before and after the heat treatments. Indeed, since this region corresponds to the condition $\omega\tau_m\approx1$, it can be calculated that $T_{\max}\sim\gamma^{-2/3}$.

The measurements are quantitatively analyzed in the framework of the tunneling model. The attenuation and the velocity are calculated numerically, using Eqs. (6) and (7). Raman processes are also taken into account, in order to describe the stronger temperature dependence above 4 K. The best fitted curves for the attenuation and velocity change are given in Fig. 3 and Fig. 4, respectively, for the data shown there. As can be seen, there is good agreement between the theoretical curves and the data. From these fits, the TS parameters $C(\sim P\gamma_l^2)$, K_3 $[\sim\Sigma(\gamma_i^2/v_i^5)]$ and the Raman parameter K_7 can be determined independently. The values obtained from attenuation measurements are given in Table II. The table contains also the values for the density of states P and the coupling parameter γ_l. These parameters are deduced from C and K_3, using the expression $\gamma_t^2/v_t^2=\gamma_l^2/v_l^2$ which is found to be valid for most of the amorphous solids,[11] and with $v_l=5750$ m/s, $v_t=3840$ m/s. The parameters $C, K_3, P\gamma_l^2, \gamma_l, P$ have also been determined from the variation of the velocity and their changes with heat treatment are in agreement with those deduced from the ultrasonic attenuation data. The absolute values of the parameters derived from attenuation measurements on one hand and from the variation of the velocity on the other hand differ by a certain factor, as is also found in amorphous solids. This has been discussed in more detail in Ref. 4.

TABLE II. TS parameters derived from ultrasonic attenuation measurements in neutron-irradiated quartz (dose 1.2×10^{19} n/cm^2) after heat treatment; $f=648$ MHz. The accuracy for C and $P\gamma_l^2$ is 10%, for K_3 and γ_l: 20%, for P 25%. K_7, is of the order of 10^2.

Parameter	Before heat treatment	300 °C 1 h	400 °C 1 h	530 °C 1 h	590 °C 1 h	700 °C 1 h
C (10^{-6})	42	42	42	38	30	19
K_3 (10^7 K^{-3} s^{-1})	12	12	12	11.1	9.1	8.8
$\overline{P\gamma_l^2}$ (10^6 g cm^{-1} s^{-2})	37	37	37	33	26	17
γ_l (eV)	0.6	0.6	0.6	0.59	0.53	0.52
$\overline{P}$ (10^{30} cm^{-3} erg^{-1})	40	40	40	39	36	24

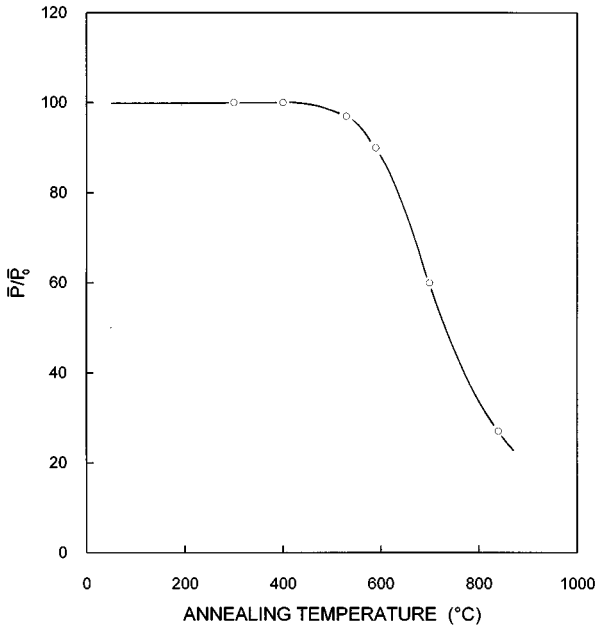

FIG. 5. Fraction of the density of states that is left after heat treatment as a function of temperature for neutron-irradiated quartz N4 (the duration of the heat treatments was 1 h for the heat treatments at 300–700 °C and 15 min for the annealing at 840 °C).

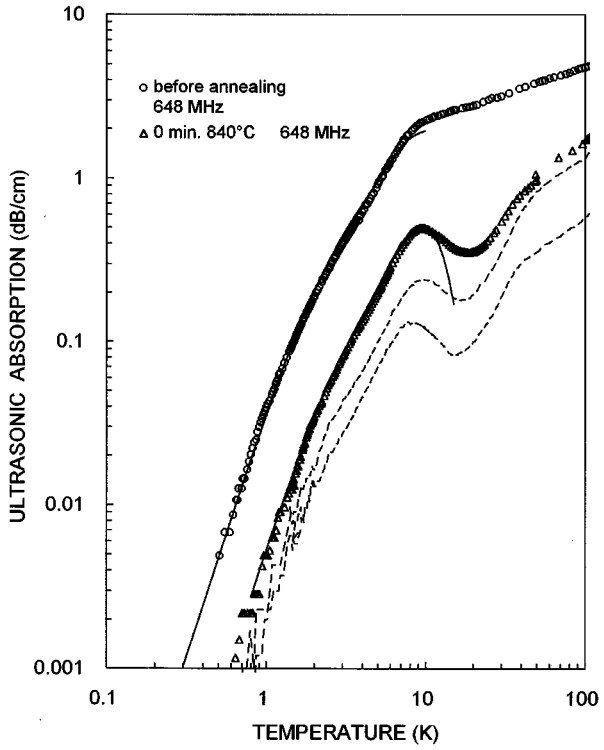

FIG. 6. Ultrasonic attenuation measurements in neutron-irradiated quartz N4 (dose 1.2×10^{19} n/cm^2) before (top curve) and after annealing at 840 °C (bottom curve). The data obtained after heat treatment for 15 min, which have been reported before in Ref. 18 are added in dotted lines: top curve for 648 MHz, bottom for 420 MHz. — : fitcurve.

Comparing the parameters obtained after heat treatment with the values obtained before heat treatment, we observe a slight decrease of P and γ_l after annealing at 530 °C, which becomes more significant after heat treatment at 590 and 700 °C. At 590 °C, already 10–15 % of the TS has disappeared, at 700 °C, the density of states decreases with about 40%. The changes in γ_l are much smaller: after heat treatment at 700 °C, the attenuation measurements show a decrease in γ_l of about 13%. The $\Delta v/v$ measurements also indicate a slight decrease of K_3, and thus γ_l, with heat treatment. This is in agreement with previous results:[15] a systematic study of the TS as a function of the neutron dose revealed that γ_l increases with increasing radiation. Here we come to a similar conclusion: after annealing, the damage in the samples decreases, resulting in a decrease of the coupling between the TS and the phonons.

Figure 5 shows the fraction of the density of states that is left after heat treatment as a function of the annealing temperature, as derived from the attenuation measurements. It is remarkable that P starts to decrease significantly from a temperature which is close to the α-β transition temperature. This transition occurs in unirradiated quartz at 573 °C, where the trigonal symmetry of the α configuration turns into the hexagonal β structure. It is known that neutron irradiation affects this transition: for doses above 6×10^{19} n/cm^2, no α-β transition is observed (quartz irradiated with such a dose shows already a hexagonal symmetry before heat treatment[9]). The fact that the influence of heat treatment seems to become important when the temperature approaches the α-β transition is interesting in view of the microscopic origin of the TS. In a recent paper,[8] we gave evidence that at least part of the TS is related to radiation induced α_1-α_2 twins. These twins consist of regions of SiO_4 tetrahedra which are 180° rotated with respect to each other and were proposed by Comes, Lambert, and Guinier[17] to explain the damaged ''crystalline'' structure of neutron-irradiated quartz. Breaking of bonds is not required for this twin formation: small displacements of approximately 0.4 Å cause the passage of chains of tetrahedra from their original α configuration to the opposite one. These irradiation-induced displacements are essentially the same as those which are observed in an unirradiated crystal near the α-β transition.[16] As the transition temperature $T_{\alpha\text{-}\beta}$ (573 °C) is approached, a dense network of Dauphiné twins is formed, the domain size becoming smaller with increasing temperature,[8] while heating above $T_{\alpha\text{-}\beta}$ gradually removes the twins.[17] When annealing an irradiated quartz sample that contains statically induced twin domains, we can thus expect some influence of heating at or above $T_{\alpha\text{-}\beta}$. This is indeed what we observe here: while heat treatment at temperatures below the transition temperature does not reveal any change, a noticeable decrease of P is observed when the heat treatment is carried out at temperatures approaching and above $T_{\alpha\text{-}\beta}$.

2. Heat treatments at 840 °C

Figure 6 shows the attenuation before and after heat treatment at 840 °C. The attenuation has been measured for K2N2 at 648 MHz and for K2N1 at 648 and 420 MHz. K2N1 was kept at 840 °C for 15 min, K2N2 was immediately cooled. From this figure, a drastic decrease of the attenuation after heat treatment, as observed for lower anneal-

TABLE III. TS parameters derived from ultrasonic attenuation measurements in neutron-irradiation quartz (dose: 1.2×10^{19} n/cm^2) after heat treatment at 700 °C (f=648 MHz) and 840 °C (648 MHz: K2N2 and K2N1; 420 MHz; K2N1). The accuracy for C and $P\gamma_l^2$ is 10%, for K_3 and γ_l: 20%, for P 25%. K is of the order of 10^2.

Parameter	Before heat treatment	700 °C 1 h	700 °C 2 h	700 °C 3 h	700 °C (K2N2) 14 h	840 °C (K2N2)[b] (a)	840 °C (K2N1)[b] 15 min	840 °C (K2N1) 15 min
C (10^{-6})	42	19	16	16	13	12	6.1	5.0
K_3 (10^7 K^{-3} s^{-1})	12	8.8	8.8	8.8	8.8	5.9	5.9	6.3
$\overline{P\gamma_l^2}$ (10^6 g cm^{-1} s^{-2})	37	17	14	14	11	10	5.3	4.4
γ_l (eV)	0.60	0.52	0.52	0.52	0.52	0.44	0.43	0.44
$\overline{P}$ (10^{30} cm^{-3} erg^{-1})	40	24	20	20	16	22	11	8.9

[a]K2N2 was heated up to 840 °C and then immediately cooled.
[b]These data have been reported before in Ref. 18 but are added for the sake of completeness.

ing temperatures, is clearly seen. The T^3 dependence at the lowest temperatures, which is frequency independent as shown by the measurements in K2N1, indicates that after both heat treatments, there are still TS left. There is, however, a significant difference with previous observations. Instead of the plateau, predicted by the tunneling model, the curves after heat treatment at 840 °C show a maximum around 10 K. This maximum is related to a particular effect of annealing on the distribution of the TS parameters and has been extensively discussed in a previous paper.[18] In that paper, we propose a slight modification of the tunneling model with a uniform but restricted λ distribution. Using the modified model, a consistent quantitative analysis of these measurements can be obtained. This imposed ''cutoff'' in the distribution of λ can be described with an extra parameter $(\tau_m/\tau)_{\min}$ and implies that the broad distribution of relaxation times, which is typical of the tunneling states, is also restricted: TS with long relaxation times vanish after heat treatment. Since this has all been explained in Ref. 18, we will not go into the details of the modified model in the present discussion, which concerns mainly the influence of heat treatment on the density of states P of the TS and on the coupling parameter γ_l. Figure 6 also shows the fitcurves obtained from numerical calculations with the tunneling model. The parameters derived from these fits are given in Table III together with those from a study at 700 °C as a function of the duration of the heat treatment which will be discussed furtheron. Note that, although the fits were determined independently, we find within the experimental accuracy the same parameters for the measurements in K2N1 carried out at different frequencies. A comparison with the data before heat treatment learns that heating up to 840 °C reduces P to half the original value. A less drastic, but nevertheless significant, decrease is found for the coupling parameter γ_l. The length of the heat treatment has also a considerable influence: when the sample is kept for 15 min at 840 °C, P decreases with another 50%. Comparing the values from Table III with those from Table II, we can conclude that the TS parameters derived after heat treatments at 700 °C (1 h) and 840 °C agree well with each other. The decrease of γ_l observed in the 840 °C measurements confirms the slight changes in γ_l found at lower annealing temperatures. And the decrease of P observed at 700 °C (1 h) is followed at 840 °C. We note however that heating up to 840 °C followed by immediate cooling has about the same effect on the density of states of the TS as a 1 h heat treatment at 700 °C.

3. Influence of the duration of the heat treatment on the TS

In order to study into more detail the influence of the length of the heat treatment, K2N3 has been further annealed at 700 °C. At first, two additional treatments of 1 h were carried out, finally, the sample was kept for 11 h at 700 °C, resulting in a total annealing time of 14 h. After each heat treatment, the ultrasonic attenuation has been measured as a function of temperature for a frequency of 648 MHz. Figure 7 shows the data for 1 and 14 h. This figure shows that the

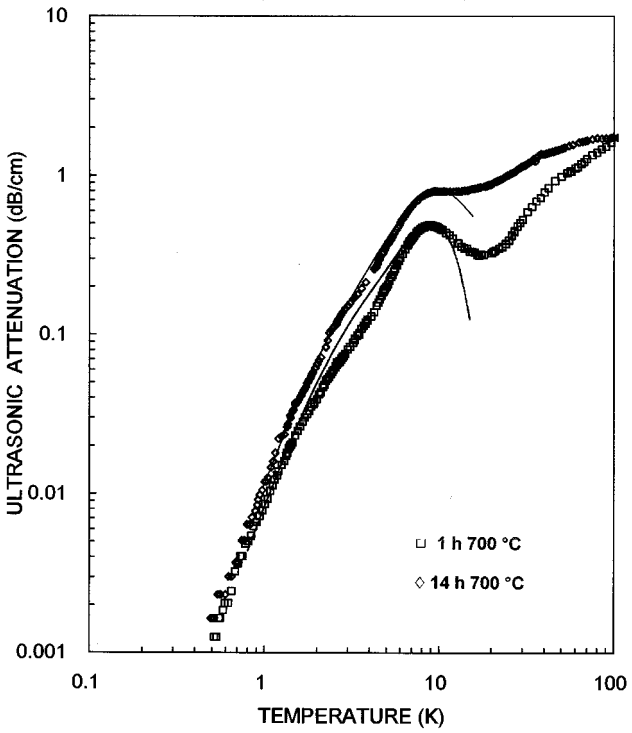

FIG. 7. Ultrasonic attenuation measurements in neutron-irradiated quartz N4 (dose 1.2×10^{19} n/cm^2) after heat treatment at 700 °C, for 1 h (upper curve) and 14 h (lower curve). Frequency: 648 MHz. — : fitcurve.

absorption decreases further as the annealing goes on, but even after 14 h of heat treatment, we observe the T^3 behavior at the lowest temperatures, indicating that there are still TS left. The maximum that appears around 10 K is similar to the observed maximum after heat treatment at 840 °C. As mentioned above, it indicates that the distribution of the TS parameters changes after annealing, as already mentioned above and is discussed in detail in Ref. 18. The best fitted curve for the given annealing time is shown in Fig. 7, Table III gives the derived parameters. As discussed above, P decreases with 40% after 1 h at 700 °C. Table III shows that another 10% disappears after 2 h annealing and after 14 h of heat treatment, we find a total decrease of 60% of the density of states. P is thus largely affected by a prolonged heat treatment, however, the remaining 40% which is left after 14 h may indicate that after a heat treatment at 700 °C not all TS will disappear, whatever the annealing time. Before discussing this in more detail, it is interesting to compare these results with the parameters obtained from heat treatment at 840 °C. We found that heating up to 840 °C anneals 50% of the TS (which requires 2 h heat treatment at 700 °C) and after 15 min annealing at 840 °C, only 25% of the TS is left. Thus both temperature and time have an influence on the density of states. The higher the temperature of the heat treatment, the lower the time required to anneal a given TS fraction.

In the following, we will try to relate the above observations with the induced structural changes. The sample discussed so far was irradiated with a dose of 1.2×10^{19} n/cm^2, which is situated well below the threshold dose mentioned by Mayer and Lecomte.[9] After heat treatment, the sample is thus expected to return to the crystalline state. This is indeed confirmed by the mass density: after the heat treatments, the mass density ρ was found to be the same as for unirradiated quartz (see Table I). However, our ultrasonic measurements still show a typical ''glassy'' behavior, due to the remaining TS. A possible interpretation of this ''incomplete'' return to the crystalline phase can be given in terms of the created disordered regions and their overlap. According to Grasse *et al.*,[19] high energetic neutrons create defective regions with a glassy structure and a density less then the crystal. For relatively low doses, they form ''islands'' in the crystalline matrix. With increasing dose, these regions grow in number, and will tend to overlap. Since the creation of these domains occurs at random, the probability of overlapping exists at relatively low doses. It is however a very small probability, involving only a small fraction of the sample, so that this overlap will not be observed in the density of the sample. The disorder of these overlapping regions will then be too high to return to the crystalline structure after annealing, and these clusters will rather evolve to a-SiO_2. This idea has been put forward before by Laermans *et al.*[20] to explain the results of positron annihilation experiments after annealing of a sample irradiated with a dose of 1.0×10^{19} n/cm^2 (similar to our N4). The heat treatment of that sample yielded a drastic increase of the long-lifetime component intensity. The result was rather unexpected, because the mass density of the sample recovered on annealing, as expected, to the value of a nonirradiated crystal and in nonirradiated α crystals, the long-lifetime component is absent. It could be understood by overlap of a minor part of the radiation-induced defective regions, which will not be removed by annealing and can give rise to the long lifetime, typical of a-SiO_2.

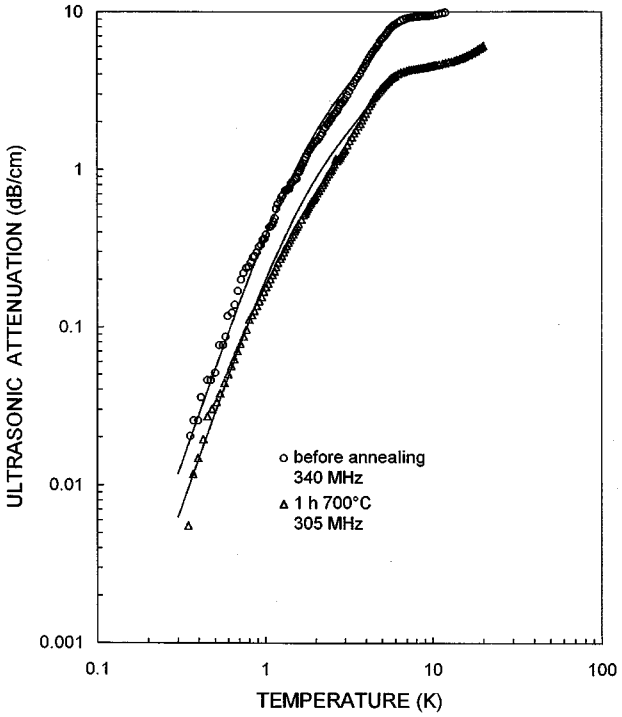

FIG. 8. Ultrasonic attenuation measurements in neutron-irradiated quartz N6 (dose 4.7×10^{19} n/cm^2) before (upper curve) and after heat treatment (lower curve) at 700 °C for 1 h. — : fit-curve.

B. Ultrasonic attenuation and velocity measurements after heat treatment for a dose of 4.7×10^{19} n/cm^2: The influence of heat treatments for a dose in the threshold region

The heat treatments discussed so far were carried out for a relatively low dose, situated well below the ''threshold region.'' The behavior of these samples after heat treatment is indeed to a large extent in agreement with the predictions based on structural studies of Mayer and Lecomte:[9] the mass density increased to that of unirradiated quartz and although we find that still 25% of the TS is left, there is a clear tendency to return to the crystalline state. In what follows, we will discuss ultrasonic measurements after heat treatment for a dose of 4.7×10^{19} n/cm^2 (labeled N6).[21] This dose is situated in (or near) the ''threshold region'' around 6×10^{19} n/cm^2, put forward by Mayer and Lecomte. The heat treatments are carried out under similar conditions as the heat treatments for the dose N4 (1.2×10^{19} n/cm^2) discussed above, so that reliable comparisons can be made.

The heat treatments discussed in this section are carried out on two samples (labeled K4N2 and K4N4), simultaneously irradiated in the same reactor and during the same cycle as the dose N4 discussed above. K4N4 was subsequently annealed for 1 h at 300, 400, 530, and 590 °C before being heat treated for different times at 700 °C; the heat treatments at 840 °C (for 15 min and 1 h) have been carried out on K4N2. After each heat treatment, the ultrasonic attenuation and velocity change have been measured as a func-

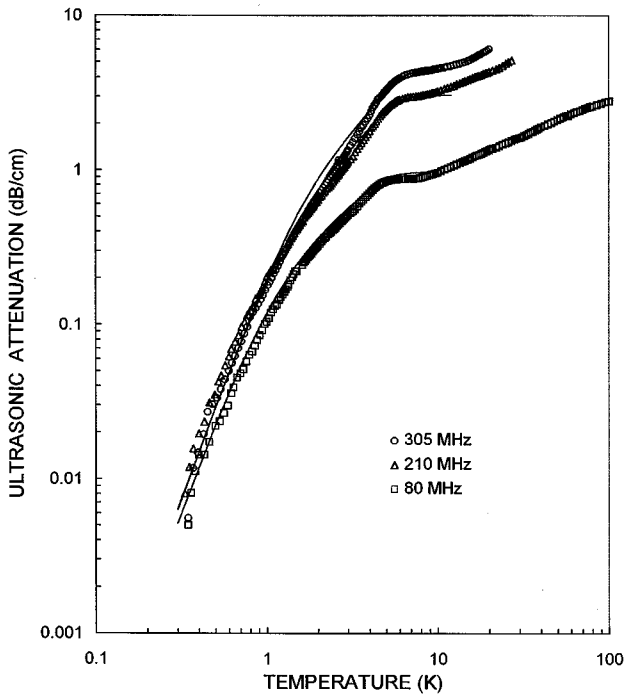

FIG. 9. Ultrasonic attenuation measurements in neutron-irradiated quartz N6 (dose 4.7×10^{19} n/cm^2) after heat treatment at 700 °C for 1 h, at different frequencies. — : fitcurve.

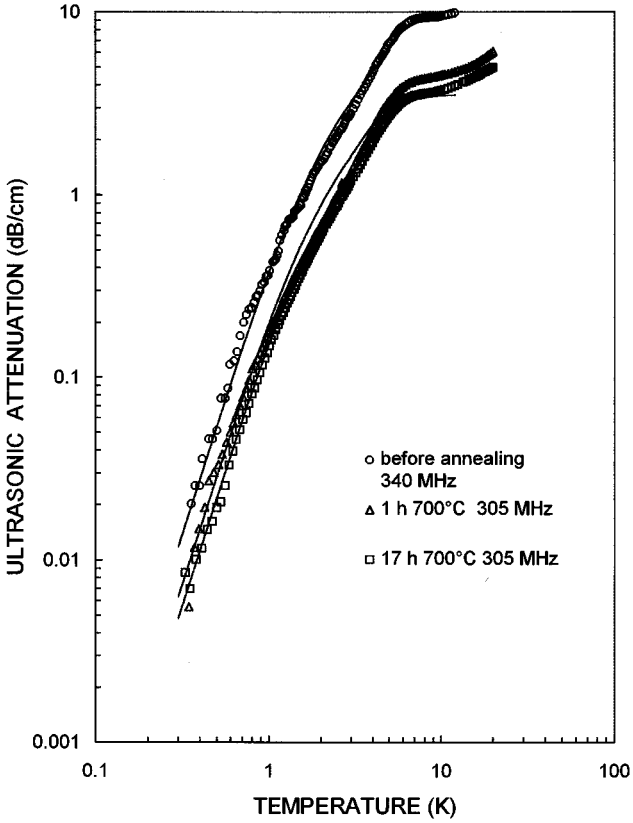

FIG. 10. Ultrasonic attenuation measurements in neutron-irradiated quartz N6 (dose 4.7×10^{19} n/cm^2) before (upper curve) and after heat treatment at 700 °C for 1 h, and 17 h (lower curve). — : fitcurve.

tion of temperature, for different frequencies. In addition, the density of the samples has been measured after each annealing (see Table I).

Figure 8 shows the ultrasonic attenuation before and after heat treatment for 1 h at 700 °C, at comparable frequencies. It is clear that the absorption strongly decreases after this annealing. But, as was also the case for the lower dose N4, the typical TS behavior is conserved: a T^3 dependence at the lowest temperatures, that levels off to a temperature-independent plateau. Figure 9 gives the attenuation after a 1 h heat treatment at 700 °C for three different frequencies and shows that the attenuation is still in agreement with the tunneling model: the T^3 behavior is independent of the frequency while the plateau increases linearly with frequency. This indicates that there are still TS left after heat treatment. However, the clear decrease of the attenuation over the whole temperature range probably means that the number of TS is reduced.

Figure 10 shows the attenuation curves after heat treatment at 700 °C for 1 and 17 h. The data for 2 h are coincident with those for 1 h. Annealing for 2 h means that after the first heat treatment of 1 h, the sample was annealed for one more hour. An additional heat treatment of 15 h resulted in the total annealing of 17 h. Whereas after 1 h at 700 °C, the height of the plateau is only 50% of the value before annealing, it is found that an additional heat treatment for 1 h at 700 °C induces no further significant changes. To verify if the TS could be further annealed at 700 °C, a longer heat treatment of 17 h has been carried out. This causes an additional decrease of the attenuation. After each heat treatment, attenuation measurements are carried out at several frequencies and all data show the typical frequency dependence expected from the tunneling model and confirm the decreasing tendency.[22]

The curves obtained before and after the different heat treatments have, within the experimental accuracy, the same shape. This means that heat treatment induces no significant changes in the coupling parameter K_3, which determines the shape of the curves in the transition from the T^3 behavior to the plateau. Thus, the observed decrease is mainly due to a decrease of the parameter C, indicating that the density of states of the TS is significantly reduced by the heat treatment. This implies that the sample has a tendency to return to the crystalline phase.

In Fig. 11 the velocity change is plotted as a function of temperature, before and after annealing at 700 °C for 1 and for 17 h, with reference temperature $T_0=0.32$ K. The qualitative behavior is the same after annealing than before. It is quite clear that the velocity change decreases with heat treatment: after heat treatment for 1 h, the slope of the logarithmic increase has lowered with 50%; after heat treatment for 17 h, we observe a further decrease, and the velocity change between 0.3 and 1 K is only 35–40 % of $\Delta v/v$ prior to heat treatment. This is consistent with the results obtained from the attenuation measurements and confirms that the density of states P of the TS is considerably reduced after annealing. From the velocity curves, it is also clear that the coupling of the TS with the phonons is not considerably affected by heat

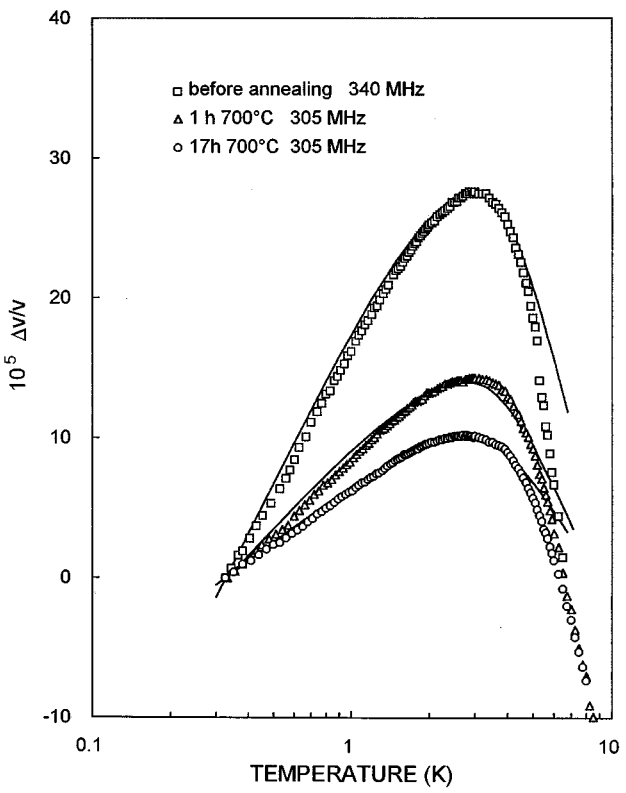

FIG. 11. Ultrasonic velocity change measurements in neutron-irradiated quartz N6 (dose 4.7×10^{19} n/cm^2), before (upper curve) and after heat treatment at 700 °C for 1 h and 17 h (lower curve). A heat treatment at 840 °C for 15 min resp. 1 h gives almost the same result as 700 °C, 1 h resp. 17 h. — : fitcurve.

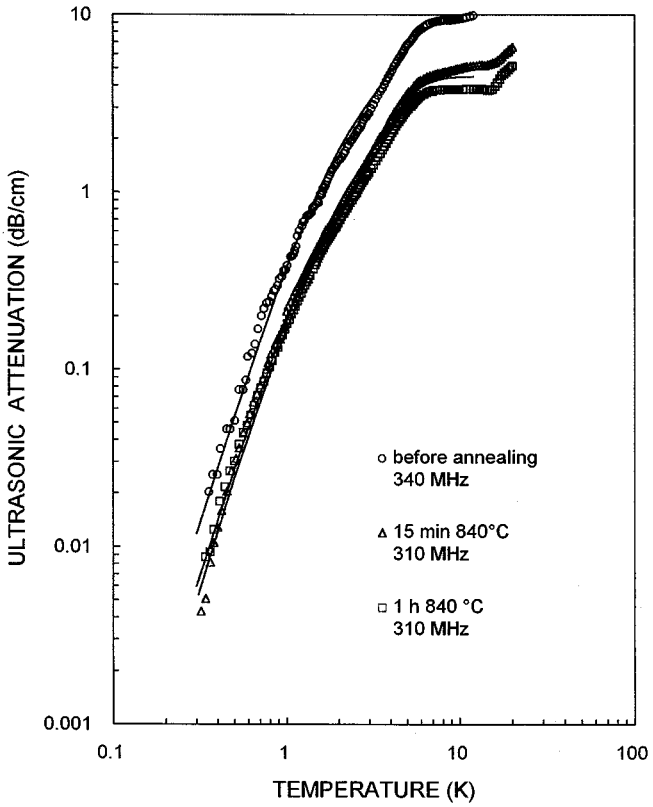

FIG. 12. Ultrasonic attenuation measurements in neutron-irradiated quartz N6 (dose 4.7×10^{19} n/cm^2) before (upper curve) and after heat treatment at 840 °C for 15 min and 1 h (lower curve). — : fitcurve.

treatment. As mentioned above, the temperature at which the maximum appears is a measure for this coupling.

Figure 12 shows the attenuation, measured before and after heat treatment for 15 min and for 1 h at 840 °C. These measurements again show a considerable decrease of the absorption over the whole temperature range. After heat treatment for 15 min, the attenuation at the plateau is only 50% of the plateau prior to heat treatment, and decreases further when the annealing is prolonged to 1 h. Since the shape of the curve is the same before and after heat treatment, this decrease can again mainly be attributed to a decrease of the density of states of the TS.

Similar conclusions can be drawn from the velocity measurements after heat treatment which were carried out after a heat treatment of 15 min and 1 h at 840 °C. The data are not given but coincide almost completely with those of the 700 °C, 1 and 17 h sample, respectively. Between 0.3 and 1 K, the velocity change decreases with about 50% after heat treatment for 15 min, and with an additional 15% when the heat treatment is prolonged to 1 h. The maximum appears for all curves at the same temperature, indicating that the coupling does not change significantly after heat treatment. Therefore, the observed decrease has to be attributed again to a decrease of P, the density of states of the TS.

It is interesting to remark that both the attenuation and the velocity curves obtained after 1 h at 700 °C coincide with the measurements after 15 min at 840 °C, and that the data obtained after 17 h at 700 °C are within experimental accuracy the same as the results after 1 h at 840 °C. It indicates that the time required to anneal a given fraction of tunneling states decreases when the temperature of the heat treatment increases. The same qualitative behavior has been observed for the lower dose N4 (1.2×10^{19} n/cm^2) (see Sec. III A).

Figures 8–12 also show the best fitted curves for the ultrasonic attenuation and velocity change before and after the different heat treatments of the specimens K4N2 and K4N4. They are obtained from the same numerical fit procedure used for the analysis of the results for the lower dose N4 in Sec. III A and allow us to derive the TS parameters.

Table IV gives the values obtained from the attenuation measurements after heat treatment at 700 and 840 °C. Again the relevant parameters have been deduced also from the variation of the velocity data and the relative changes with heat treatment are in agreement with those found from attenuation measurements. Considering the heat treatment after 1 h at 700 °C, we see that the TS parameters derived from attenuation measurements at different frequencies agree with each other. Compared to P prior to heat treatment, the density of states is reduced with 50%. The coupling parameter γ_l is not affected, which implies that the remaining TS are similar in nature to the TS before annealing; this will be further discussed in the next section (C). The attenuation curve after 2 h of heat treatment at 700 °C coincides with the absorption after 1 h annealing, and results indeed in the same TS parameters. However, an additional heat treatment, resulting in a total annealing of 17 h at 700 °C, shows a further decrease

TABLE IV. TS parameters derived from ultrasonic attenuation measurements in neutron-irradiated quartz (dose: 4.7×10^{19} n/cm^2) after heat treatment at 700 and 840 °C. The accuracy for C and $\overline{P}\gamma_l^2$ is 10%, for K_3 and γ_l: 20%, for P 25%. K_7 is of the order of 10^2.

Parameter	Before heat treatment 340 MHz	1 h, 700 °C 80 MHz	1 h, 700 °C 210 MHz	1 h, 700 °C 305 MHz	2 h, 700 °C 340 MHz	17 h, 700 °C 310 MHz	15 min, 840 °C 310 MHz	1 h, 840 °C 305 MHz
C (10^{-6})	371	164	198	199	178	153	195	169
K_3 (10^7 K^{-3} s^{-1})	15	15	16	15	15	15	15	15
$\overline{P}\gamma_l^2$ (10^6 g cm^{-1} s^{-2})	314	141	168	171	153	131	143	122
γ_l (eV)	0.68	0.68	0.69	0.68	0.68	0.68	0.67	0.68
$\overline{P}$ (10^{30} cm^{-3} erg^{-1})	266	118	136	143	131	111	143	122

of $\overline{P}$: from the attenuation, measured at two frequencies, we derive a density of states which is about 40% of the original P, but this long heat treatment has still no considerable influence on the coupling parameter. The parameters obtained from the velocity confirm this: from the $\Delta v/v$ measurements, we find a 50% decrease of P after 1 h heat treatment, another 10% vanishes after 17 h. The coupling undergoes, however, no significant changes. From the qualitative considerations, we could already derive that no big changes in γ_l would appear. The numerical analysis, however, shows that the coupling does not change at all.

The decrease in P indicates that the sample has a tendency to return to the crystalline phase after heat treatment. However, a prolongation of the heat treatment seems to induce only small changes in the density of states. It is interesting to consider this in view of the changes in the mass density. We have measured the density of our samples after each heat treatment, the found values are included in Table I: after heat treatment at 700 °C for 1 h, the mass density increased with about 1.5%. As explained above, an increasing density corresponds with decreasing radiation damage. Both the decrease in P and the increase in ρ indicate therefore a return to the crystalline state. Further heat treatments at 700 °C seem to have no significant influence on the mass density, which might be related to the relatively small changes in P after prolongation of the heat treatments.

The relative changes in the attenuation and velocity change after heat treatment at 840 °C show a close agreement: analysis of the velocity data shows that the coupling parameter remains unchanged, while the density of states is significantly reduced after heat treatment. The qualitative observation that the curves after heat treatment at 700 °C for 1 h are very similar to the measurements after annealing at 840 °C for 15 min can also be seen from our quantitative analysis: the parameters derived from the fitcurves, which are independently obtained, appear to give, within experimental accuracy, the same values for both heat treatments. The same agreement is found between the measurements after a 1 h heat treatment at 840 °C and a heat treatment at 700 °C for 17 h.[22]

C. Comparative discussion

In what follows, we will compare the results obtained from the heat treatments for the relatively low dose N4, discussed in Sec. III A, with the observations for the dose N6 in the ''threshold-region'' reported in Sec. III B. First of all, it is clear that the tunneling states anneal ''faster'' for lower doses: whereas only 25% of the TS is left after a heat treatment at 840 °C for 15 min for K2N1 (Table III), still 40% is found after the same heat treatment for K4N2 (Table IV). This agrees with the predictions of Mayer and Lecomte[9] who report that the temperature required to obtain the predicted behavior (i.e., a return to the crystalline state) increases with increasing dose. It can therefore be expected that for heat treatments at higher temperatures, a further decrease of the density of states will appear.

Contrary to the expectations, we might conclude that the samples irradiated with the high dose N6 (4.7×10^{19} n/cm^2) behaves to a large extent as the lower dose N4 (1.2×10^{19} n/cm^2), i.e., as a dose well below the threshold region. Indeed, the density of states of the TS decreases considerably after heat treatment, and the mass density increases after annealing. There are, however, some significant differences. The mass density of N4 increases to that of unirradiated quartz ($\rho=2.650$ g/cm^3), while the density of the stronger irradiated sample (N6) increases after annealing at 700 or at 840 °C only to the relatively small value of ($\rho=2.596$ g/cm^3), clearly well below the density of crystalline quartz. It is also striking that 15 min at 840 °C leaves only 25% of the TS in N4, while still 50% is left in N6. Furthermore, a significant decrease of the coupling of the TS with the phonons was observed for the dose N4, while heat treatment does not seem to affect γ_l for N6. This is quite remarkable in view of the decrease in P, which indicates that N6 has a tendency to evolve after heat treatment to the crystalline phase. As mentioned before, previous measurements in neutron-irradiated quartz as a function of the dose showed that the coupling increases with increasing dose.[15] This has been interpreted in terms of the evolution of neutron-irradiated quartz to vitreous silica: since the coupling between the phonons and the TS in irradiated quartz is only slightly different from that in

TABLE V. Value for the coupling parameter γ_l (eV) derived from attenuation measurements before and after heat treatment in neutron-irradiated quartz.

Dose (n/cm^2)	K9 0.85×10^{18}	N4 1.2×10^{19}	N5 2.6×10^{19}	N6 4.7×10^{19}
Before anneal	0.51 (Ref. 4)	0.60	0.62 (Ref. 25)	0.68
1 h 590 °C		0.53		
1 h 700 °C		0.52		0.68
15 min 840 °C		0.43		0.68

vitreous SiO_2, it has always been suggested that the TS in both forms of SiO_2 are *similar* in nature.[23,24] However, as discussed in Ref. 18, the coupling is not ''the same.'' With increasing irradiation (and thus with increasing damage), the TS are slightly modified and the coupling evolves to that of a-SiO_2. The changes in the TS and their coupling with the phonons can then be understood in terms of the disorder and the local arrangement of the environment of the TS. Table V summarizes the values for the coupling parameter found for different doses as well as the values found after heat treatment for N4 and N6, derived from the attenuation measurements. It clearly shows the increasing tendency of γ_l with increasing dose, the decrease after heat treatment for the dose N4 and the constant coupling observed after heat treatment for N6. In view of the discussion above, the decreasing coupling after heat treatment of N4 can be understood as an indication of decreasing damage and thus as a return to the crystalline state, in agreement with the observed decrease in P. The tunneling states change because of the heat treatments and behave as the TS in a less disordered environment. However, whereas the decrease in the density of states after heat treatment for the dose N6 also indicates a return towards the unirradiated crystal, the coupling remains constant. This might indicate that for this dose, the nature of the TS remaining after heat treatment is the same as before annealing. In other words, it suggests that the local environment of the TS that are left is the same as before the heat treatment; the number of tunneling states is reduced after annealing, but the TS that are still left are ''the same'' as before.

We can relate this to another striking difference in the behavior after heat treatment of both doses. As discussed in Ref. 18, heat treatments at 840 °C and prolonged heat treatments at 700 °C induce a maximum in the ultrasonic attenuation, which can be described by modifying the distribution of the TS parameter λ. After similar heat treatments for the dose N6, such a maximum does not appear, indicating that no important changes in the λ distribution are induced. Since the parameter $\lambda = d(2mV/\hbar^2)^{1/2}$ is related to the mass m of the tunneling particle, the distance d between the minima of the well and the barrier V, changes in the λ distribution imply changes in the nature of the tunneling entity. From this point of view, it can be expected that the coupling of these ''modified tunneling states'' with the phonons might get influenced as well. This hypothesis finds support in our observations: annealing of the dose N4 gives evidence for a modification of the tunneling entity and reveals changes in the coupling parameter γ_l, whereas the heat treatments for the dose N6 induce no significant changes in the coupling nor in the distribution of λ.

In an attempt to correlate those observations with the model for the tunneling states which we gave in Ref. 8 and in short described above in Sec. IV A, it has to be remarked that in the case of the lower dose N4 the chains of rotated tetrahedra will be more hindered after heat treatment because of the increase of the order in the sample, reflecting itself in the recovery of the mass density to the value before irradiation. Such a distinct recovery is not the case for N6: for this dose the TS are found to remain ''the same,'' as seen above. The observation of a maximum in the ultrasonic attenuation for N4 after heat treatment, which was interpreted in terms of a cut off the λ distribution (restriction to lower values) shows that the random distribution of the TS is changed, e.g., the size of the microtwin domains is modified and restricted to particular values. In view of the fact that $\lambda = d(2mV/\hbar^2)^{1/2}$, we suggest that the probable mechanism is the disappearance of the TS with the large mass. At the α-β transition (573 K) a dense network of α_1-α_2 microtwins is formed which may not fully disappear upon cooling. As a consequence after the heat treatment the relative contribution of small microtwins will be higher than before.

In order to confirm the above arguments, further heat treatments can give interesting information. Extending the annealing of N6 to longer heat treatments and higher temperatures might reveal a maximum in the attenuation, giving evidence for changes in the distribution of the TS parameters. It would then also be appropriate to verify if such a modification is accompanied by changes in the coupling parameter. Extending the study of the tunneling states after heat treatment to higher doses might offer an interesting tool to obtain more information about the so-called ''threshold region,'' since the dose N6 has to a large extent characteristics of a dose below this threshold.

V. SUMMARY AND CONCLUSION

In this paper, we reported a systematic study of the influence of heat treatment on the TS in neutron-irradiated quartz. Ultrasonic attenuation measurements and measurements of the velocity change have been carried out on well characterized samples, as a function of temperature in the ultrasonic frequency range (50–650 Mhz). Two doses have been studied, one situated well below the so-called threshold region and the other situated near or in this threshold region, where important structural changes start to take place. The heat treatments have been carried out at temperatures from 300 to 840 °C, for times from 0 min (immediate cooling) to 17 h. The low-temperature data, as measured after the heat treatments, still show the presence of TS, and can be theoretically described by numerical fits using the tunneling model. They allow to determine the density of states of the TS and the coupling of the TS with the longitudinal phonons. The quantitative analysis shows—at first sight—that both doses have a similar tendency: after heat treatment the density of states decreases significantly. A prolongation of the heat treatment and an increase of the annealing temperature result in a further decrease of the density of states. However, a comparison of the results for both doses also indicates some significant differences: the density of N6 increases but does not reach the value of unirradiated quartz. A significant decrease of the coupling of the TS with the phonons was observed for the dose N4, while heat treatment does not seem to affect the coupling for N6. This can be related to another remarkable difference in the behavior after heat treatment of both doses: whereas heat treatments at 840 °C and (prolonged) heat treatments at 700 °C for N4 reveal changes in the λ distribution, similar heat treatments for N6 give no indications for important changes in λ. This indicates that for the latter, the nature of the TS after heat treatment is the same as before annealing, while for the lower dose, heat treatment does not only

influence the number of TS, but also modifies the tunneling entity itself.

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