

Low-temperature specific heat and thermal conductivity of neutron-irradiated crystalline quartz

J. W. Gardner and A. C. Anderson

Physics Department and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The specific heat C and thermal conductivity κ of neutron-irradiated crystalline quartz have been measured to $\lesssim 0.1$ K. Four types of low-energy excitations are observed, two of which may be removed selectively by heat treatment. From the C and κ of annealed samples it is shown that the localized excitations found in vitreous silica also occur in neutron-damaged quartz. These excitations cause the unusual low-temperature behavior which is characteristic of amorphous materials. The properties of these excitations appear to remain unchanged as the total density of excitations is reduced by a factor of ≈ 40 . At greater dilution, the localized excitations are masked by the effects of other, unidentified excitations.

INTRODUCTION

The low-temperature properties of amorphous materials are characteristically different from those of the crystalline state¹ and are believed to be caused by a broad spectrum of localized, low-energy excitations. The behavior of these excitations is accounted for by a phenomenological theory that involves two-level, quantum-mechanical tunneling of some entity between neighboring potential-energy minima.^{2,3}

A microscopic description of such a localized excitation has not been determined for any amorphous material. Hence, some attention has been directed to disordered crystalline materials exhibiting the same low-temperature properties. It is thereby hoped that, with a greater understanding of crystalline environments, the excitation might be identified. Several crystalline systems have been studied, including β -alumina,⁴⁻⁹ Li_3N (Refs. 9-11), NbZr (Refs. 12, 13), neutron-irradiated quartz,¹⁴⁻¹⁷ and other materials.¹¹ The purpose of the present paper is to provide additional information on neutron-irradiated quartz.

The first low-temperature measurements on neutron-irradiated quartz¹⁴ were of thermal conductivity κ at temperatures $T \gtrsim 3$ K. With increasing irradiation, the thermal conductivity decreased and began to display near 10 K a region or "plateau" nearly independent of temperature. Such plateaus in κ are characteristic of the amorphous state, and the apparent formation of a plateau was the incentive for starting the present measurements. Meanwhile, additional information has become available. The thermal conductivity measurements were extended¹⁶ down to ≈ 1.4 K. At the lowest temperature, κ approached the T^2 temperature dependence characteristic of glasses. Ultrasonic measurements exhibited additional behavior characteristic of glasses, namely phonon echos¹⁷ and saturation of attenua-

tion.¹⁵ In our measurements discussed below, the thermal conductivity has been extended to below ≈ 0.1 K, and the presence of a T^2 temperature dependence is confirmed. Also, specific-heat measurements have been carried out down to ≈ 0.1 K. A contribution to the specific heat is found which is linear in temperature as for a glass. Furthermore, the specific heat and the thermal conductivity appear to scale under different irradiation dosages as would be expected if both properties were associated with the same set of excitations. Thus, not only does neutron-damaged quartz behave like a glass, but it would appear that the magnitude of the glasslike properties can be varied systematically by increased exposure to neutron radiation.

We have been cautious in making the foregoing statements because certain problems prevent a more definitive conclusion. Neutron irradiation of crystalline quartz produces not only a broad spectrum of low-energy excitations similar to that found in vitreous silica, but also a discrete spectrum of excitations giving rise to a Schottky peak in the specific heat at 1 K, another broad spectrum said to be associated with Al impurities and activated by γ irradiation, and a third rather broad spectrum activated by thermal treatment. As various of these excitations contribute to the measured low-temperature properties in this and other investigations, they are discussed here in some detail to provide a guide for future research. Since several types of excitations must be discussed, we will indicate those associated with glasslike behavior as TLS (two-level state) excitations, as has been done previously in the literature.

EXPERIMENTAL DETAILS

Five samples measuring $1 \text{ cm} \times 0.4 \text{ cm} \times 5 \text{ cm}$ and having a mass of ≈ 5 g were cut from the same crystal¹⁸ of electronic-grade, cultured α -quartz.

The 5-cm dimension was parallel to the c axis. From previous experience,¹⁹ it was felt that these crystals would be more reproducible than natural crystals. It is not known if, for low-temperature measurements, this was a reasonable assumption.

One sample was reserved as a reference and four were irradiated in the CP-5 reactor at Argonne National Laboratory for 3, 27, 270, and 2100 h, respectively. The samples will therefore be designated as 0 h (unirradiated), 3 h, 27 h, 270 h, and 2100 h throughout this paper. For the irradiation, the samples were wrapped in aluminum foil and placed in aluminum cans. The cans were perforated, hence the samples were in direct contact with the cooling water of the reactor. Table I lists the dose received by each sample in different energy ranges. As the mean free path of a neutron in SiO_2 is ≈ 10 cm, the samples were irradiated uniformly. The γ exposure was $\approx 10^6$ R/h; the β exposure is not known. Following irradiation, the samples were etched to remove surface contamination.

Before irradiation the samples (upon wetting the optically rough surfaces) were colorless and transparent to the eye. After irradiation the 2100-h sample was uniformly bluish, the 270 h was uniformly light tan, the 27 h was dark tan in a central trapezoidal region (see inset of Fig. 1) and light tan outside this region, and the 3-h sample was smoke colored in an identical central region and clear outside. The color patterns of the 27-h and 3-h samples were not caused by an inhomogeneous exposure in the reactor. Also, the impurity content in the central region did not differ significantly from that in the outer region. The visual appearances are summarized in Table

I, along with mass densities measured to an accuracy of 0.1%

Measurements were also made on samples after heat treatment at 370 °C again at 840 °C in an argon atmosphere. For the 370 °C anneal, the sample was brought to temperature in 15 min, held at 370 °C for ≈ 2 h, then cooled to room temperature in ≈ 20 min. For the 840 °C anneal, the sample was brought to temperature in ≈ 1 h, then allowed to cool, reaching 500 °C in 20 min and ≈ 200 °C in 1.5 h. Color and density changes of the heat-treated samples are listed in Table I.

Thermal conductivities were measured with the heat flux directed parallel to the crystalline c axis. The temperature gradient created by the heater was measured with precalibrated Ge thermometers to eliminate uncertainty in temperatures from radioactive self-heating effects. Specific heats were measured using two techniques. One utilized a weak thermal link to the refrigerator and was operated like an "adiabatic" calorimeter.²⁰ In the other technique, one end of the sample was thermally bounded to the refrigerator. From a measurement of the thermal relaxation time of the sample and the measured thermal conductivity κ , the specific heat C could be deduced. Since the samples were self-heated by radioactive decay, the second technique allowed us to measure C to lower temperatures. However, these data were consistently high by a constant factor compared with the calorimetric data taken at higher temperatures. This may have been caused by slight cracking of the sample observed near the bond after cryogenic cycling. Hence the diffusivity data have been scaled by

TABLE I. Radiation dose, mass density, and appearance of samples after exposure to neutron irradiation and after heat treatment at 370 and 840 °C.

Sample →	0 h	3 h	27 h	270 h	2100 h
Dose (cm^{-2}), 0 → 0.5 eV		5.8×10^{17}	5.3×10^{18}	4.7×10^{19}	4.1×10^{20}
Dose (cm^{-2}), 0.5 eV → 0.1 MeV		2.2×10^{17}	2.0×10^{18}	1.9×10^{19}	1.5×10^{20}
Dose (cm^{-2}), 0.1 MeV → ∞		2.9×10^{17}	2.7×10^{18}	2.6×10^{19}	2.1×10^{20}
Density (g/cm^3)	2.651	2.648	2.640	2.517	2.256
Color	clear	central smoky	central tan	light tan	blue
After 370 °C anneal:					
Color		central		dark tan	green
After 840 °C anneal:		light gray			
Color	central blue in reflection	central blue in reflection	central blue in reflection	clear	
Density (g/cm^3)	2.651	2.650	2.650	2.520	

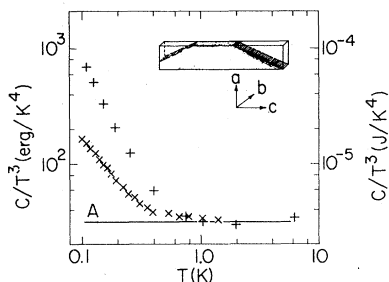


FIG. 1. Heat capacity of sample 0 h (unirradiated) plus addenda, divided by T^3 . \times —prior to heat treatment, mass of sample 5.34 g; $+$ —following heat treatment, mass of sample 5.12 g. Line A is the heat capacity of the 5.34-g sample after subtraction of the heat capacity contributed by the addenda. The inset shows the color pattern observed in the annealed 0-h sample and in the irradiated 3-h and 27-h samples.

a constant factor of 0.85–1.0.

It should be noted that quartz undergoes an α - β phase transformation at a temperature near 537°C, well under our final heat-treatment temperature of 840°C. After the measurements were completed, the (100) x-ray reflections were measured for samples heat treated to 840°C. For the 0-h, 3-h, and 27-h samples the (100) reflection was a strong narrow line characteristic of α -quartz. For the 270-h sample the (100) reflection was *nearly as narrow*, but the angle was characteristic of β -quartz. Indeed, the mass densities of samples 3 h and 27 h (heat treated to 840°C) were nearly identical to that of α -quartz, while the density of the 270-h sample was close to that of β -quartz (see Table I). The failure of the β - α phase transition to occur in samples irradiated at $\approx 5 \times 10^{19}$ cm $^{-2}$ has been noted previously.²¹ The α -phase can be restored with an anneal a factor of ≈ 100 longer than that used on the present samples.

EXPERIMENTAL RESULTS, UNIRRADIATED SAMPLE

The specific heat and thermal conductivity of the 0-h sample were measured to provide a reference against which the irradiated samples could be compared. Because of some unusual and unexpected behavior of sample 0 h, we discuss the results in detail.

Figure 1 shows the specific heat of sample 0 h plus addenda. The data have been divided by T^3 to emphasize departure from Debye behavior. The rise in C/T^3 below 1 K is consistent with our estimate of the heat capacity of the addenda. Subtracting the addenda gives line A, which corresponds to a Debye heat capacity for phonons of average velocity $\bar{v} = 4.26 \times 10^5$ cm/sec. Also shown in Fig. 1 is the heat capacity of sample 0

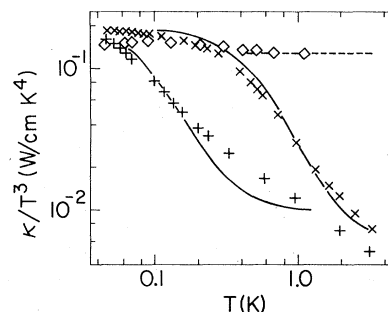


FIG. 2. Thermal conductivity of unirradiated sample 0 h, divided by T^3 to allow expansion of the vertical axis and to emphasize departures from boundary scattering. \times —central region prior to heat treatment, 0.4 cm \times 1.0 cm cross section; $+$ —central, tinted region after heat treatment, 0.4 cm \times 1.0 cm cross section; \diamond —region outside tinted area after heat treatment, 0.40 cm \times 0.45 cm cross section. The dashed line indicates κ/T^3 limited by boundary scattering for a cross section of 0.4 cm \times 1.0 cm, not corrected for phonon focusing or finite sample length. Solid curves are discussed in the text.

h after heat treatment at 840°C. There is an additional contribution to the heat capacity, this contribution having a temperature dependence of $\approx T^{0.5}$. The origin of this additional heat capacity is not known.

The thermal conductivity of sample 0 h is shown in Fig. 2. These data have been divided by T^3 to emphasize departures from a κ limited only by boundary scattering as represented by the dashed line. After heat treatment at 840°C, the thermal conductivity of the central region was reduced as shown in Fig. 2. The central region after the anneal appeared bluish in scattered light and brown in transmitted light. The shape of this region was identical to that of the irradiated 3-h and 27-h samples as shown by the inset of Fig. 1. Outside this colored central region the crystal was clear and the thermal conductivity varied as T^3 with a magnitude approximately predicted by boundary scattering²² (see Fig. 2).

The deviations from boundary scattering in the central region of sample 0 h are suggestive of phonon scattering from inclusions. Indeed, the optical appearance is also indicative of the Rayleigh scattering of light from inclusions. If a density \mathfrak{N} of spherical inclusions is assumed, all inclusions having the same radius r , the phonon mean free path as a function of phonon frequency ω would be given by $l = (l_B^{-1} + l_I^{-1})^{-1}$, where l_B is from boundary scattering and $l_I = (\mathfrak{N}\pi r^2)^{-1}$ if the phonon wavelength $\lambda \lesssim r$, and²³ $l_I \approx 9(4\pi r^2 \mathfrak{N})^{-1}(\bar{v}/r\omega)^4$ if $\lambda \gtrsim r$. The curve through the data of Fig. 2 for the sample before heat treatment gives $r \approx 80$ Å and $\mathfrak{N} \approx 2 \times 10^{13}$ cm $^{-3}$, while for the heat-treated sample $r \approx 460$ Å and $\mathfrak{N} \approx 3 \times 10^{11}$ cm $^{-3}$.

There would be sufficient Ca impurities to account for such inclusions. However, since the Ca content was uniform throughout the sample, some growth defect within the central region would be indicated.²⁴

As will be noted below, the "inclusions" also apparently increased in size with heat treatment for sample 3 h but not for sample 27 h. In addition, the increase in specific heat with anneal occurs in the 3-h sample but not the 27-h sample. (More accurately, these effects are greatly reduced in the 27-h sample.) Thus the effect of heat treatment on κ and C depends on the damage sustained under neutron irradiation.

EXPERIMENTAL RESULTS, IRRADIATED SAMPLES

The thermal conductivities of the four irradiated samples are shown in Fig. 3. The conductivity decreases with increasing irradiation except for the most irradiated sample, 2100 h, which has a larger κ than sample 270 h. The further change in κ for three of these samples after heat treatment at 840°C is shown in Fig. 4. Sample 2100 h was annealed only at 370°C, and no change in κ could be detected.

The specific heats of the four samples, divided by T^3 to emphasize departure from Debye behavior, are plotted in Figs. 5 and 6. The addenda contributions have been subtracted off. A peak occurs near 1 K which increases with irradiation except for the 2100-h sample. There is also a contribution which appears below ≈ 0.5 K and which again increases with irradiation except for the 2100-h sample.

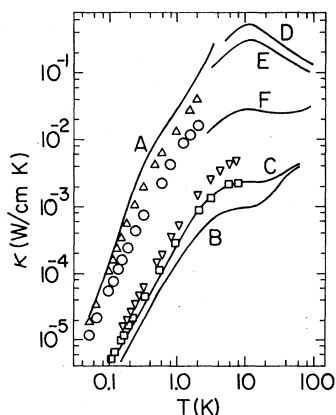


FIG. 3. Thermal conductivities of irradiated samples. Δ —3 h; \circ —27 h; \square —270 h; ∇ —2100 h. For reference: A—unirradiated sample 0 h from Fig. 2; B—vitreous silica (Ref. 30); C—neutron-irradiated vitreous silica (Ref. 30); D, E, F,—data on crystalline quartz from Ref. 14, neutron irradiated.

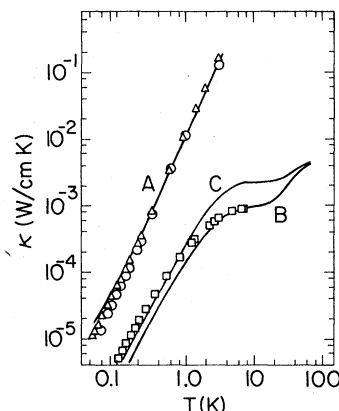


FIG. 4. Thermal conductivity of irradiated samples after heat treatment at 840°C. Same scale as Fig. 3. Δ —3 h; \circ —27 h; \square —270 h. For reference: A—unirradiated but *heat treated* sample 0 h from Fig. 2; B, C—same as Fig. 3.

After a heat treatment at 370°C, the 3-h sample showed a greater negative slope below 0.4 K but no change in the peak at 1 K. The 270-h sample, annealed at 370°C (for only 1 h), showed no change in C at any temperature. A 370°C anneal of sample 2100 h removed the peak at 1 K but did not change the C at lower temperatures (see Fig. 6).

The specific heats of samples 3 h, 27 h, and 270 h obtained after an anneal at 840°C are shown in Fig. 7. The peak at 1 K has been removed or, for the 270-h sample, reduced by a factor of 4. The specific heat below ≈ 0.4 K is nearly unchanged for sample 270 h, reduced by a factor of 3 for 27 h and *increased* by 36% for sample 3 h. The specific-heat data of 3 h are now nearly identical to those of the annealed but unirradiated

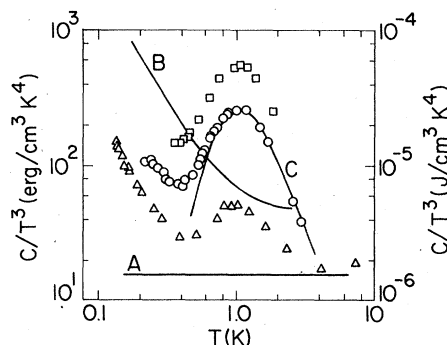


FIG. 5. Specific heat of irradiated samples, divided by T^3 to emphasize departure from Debye behavior of the undamaged crystal. Δ —3 h; \circ —27 h; \square —270 h. For reference: A—Debye phonon contribution from Fig. 1; C—calculated for a two-level Schottky peak plus phonon contribution; B—vitreous silica (Ref. 30). The specific heat of neutron-irradiated vitreous silica lies about 30% below curve B.

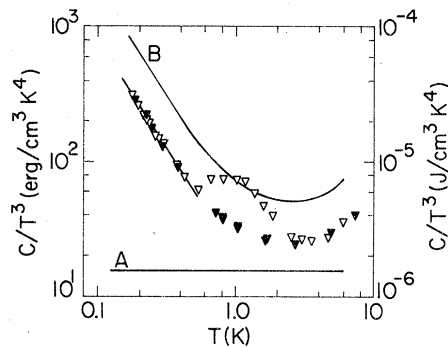


FIG. 6. Specific heat, divided by T^3 , for irradiated sample 2100 h. Same scale as Fig. 5. ∇ —before heat treatment; \blacktriangledown —following heat treatment at 370 °C. Curves A and B same as Fig. 5. Note the increased magnitude of C/T^3 for $T > 3$ K as found in vitreous silica, curve B. The curve through the data was calculated from the measured thermal conductivity of this sample as explained in the text. The mass density of sample 2100 h was close to that of neutron-irradiated vitreous silica.

crystal 0 h which are included in Fig. 7 for comparison.

We thus see, in κ and C , a complicated set of changes with neutron irradiation and heat treatment. In the next section we first discuss those changes which are of least interest to the paper but which must be “removed” in order to observe any behavior analogous to that found in amorphous systems.

In this paper we are concerned primarily with the temperature range below ≈ 1 K, since this is the range in which the TLS excitations found in amorphous materials dominate the measured properties. Nevertheless it is noted that a ther-

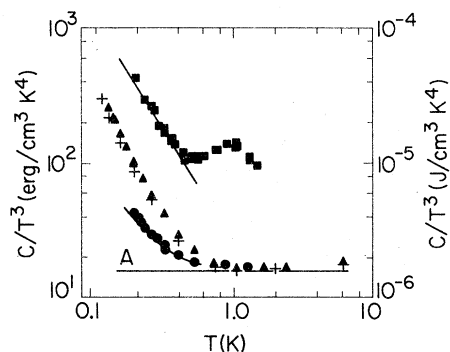


FIG. 7. Specific heat, divided by T^3 , of neutron-irradiated samples heat treated at 840 °C. Same scale as Figs. 5 and 6, \blacktriangle —3 h; \bullet —27 h; \blacksquare —270 h. For reference: $+$ —unirradiated sample 0 h after heat treatment at 840 °C; from Fig. 1, addenda contribution subtracted; A—phonon contribution. The two lines near the 27 h and 270 h data were calculated from the measured conductivities of the respective samples as explained in the text.

mal anneal at 840 °C of irradiated sample 270 h reduced the thermal conductivity in the region of the plateau ($T \gtrsim 1$ K) (see Fig. 4). This is the opposite of the effect observed in Ref. 14. The significance of this difference is not known, as the cause of the plateau is not understood. It is noted that the thermal conductivity of sample 270 h was initially smaller in magnitude than the samples of Ref. 14, presumably because of a larger neutron irradiation.

DISCUSSION

The most prominent feature of the irradiated samples is the peak in C/T^3 near 1 K. As indicated by curve C in Fig. 5, this peak is fit extremely well above 0.5 K by a two-level Schottky heat capacity having an energy splitting of 5.3 K. A Schottky peak with approximately the same splitting has been observed in a vitreous silica,^{25,26} and thus the peak may be associated with a particular defect in the SiO_2 system. Indeed, the number of Schottky excitations in sample 720 h was $2.7 \times 10^{19} \text{ cm}^{-3}$, a factor of 500 greater than the known impurity level. The number of Schottky excitations increased with irradiation for the 3-h, 27-h, and 270-h samples, but decreased for the more disordered 2100-h sample. A summary is given in Table II. Also, a 370 °C anneal removed the peak (reduction >10) from the 2100-h sample, but not the other samples. Hence the density and stability of the Schottky excitations depends on the structural condition of the SiO_2 . In the vitreous silica Suprasil W, the magnitude of the peak in C/T^3 at 1 K is reduced by heat treatment²⁶ at 1300 °C or by electron irradiation.²⁵ The peak apparently has not been observed in other vitreous silicas.

The Schottky excitations appear to interact relatively weakly with phonons. Sample 270 h had the largest peak in C/T^3 before heat treatment. After heat treatment at 840 °C the peak was reduced by almost an order of magnitude, yet the thermal conductivity near 1 K did not increase, but decreased. For samples 3 h and 27 h, the κ at the highest temperatures did increase with heat treatment, but not nearly as much²⁷ as the decrease in the magnitude of the peak in C/T^3 .

Another contribution to the specific heat expected in neutron-irradiated SiO_2 crystals is a term roughly linear in T for $T \leq 0.5$ K caused by the attendant γ radiation in the reactor. These excitations have been ascribed to Al impurity,²⁸ have been claimed to anneal out at a temperature of 350 °C, and have been shown not to affect the thermal conductivity.²⁹ The reason for our preliminary anneal at 370 °C was to remove these excitations. As discussed previously, such an

TABLE II. Number of Schottky excitations (per cm³) contributing to peak in C/T^3 at 1 K following irradiation and following heat treatment at 370 and 840 °C.

Sample →	0 h	3 h	27 h	270 h	2100 h
After irradiation	0	2.0×10^{18}	1.2×10^{19}	2.7×10^{19}	2.4×10^{18}
After 370 °C anneal	0	2.0×10^{18}		2.7×10^{19}	$<10^{17}$
After 840 °C anneal	0	$<4 \times 10^{16}$	$<4 \times 10^{16}$	5.6×10^{18}	

anneal did not alter the specific heat at $T \leq 0.5$ K for the 270-h or 2100-h samples, but did cause a small reduction for the 3-h sample. The 27-h sample was heat treated only at 840 °C, and this caused a reduction in specific heat by a factor of 3. If, from Ref. 28 we use a "width" of 6 K for this spectrum of excitations to estimate their number, we obtain ≈ 5 ppm (wt.) of Al impurity. This is in agreement with the measured value¹⁸ and suggests that this spectrum of excitations was present in our 27-h sample and, to a lesser extent, in the 3-h sample. In any event, since our final anneal was at 840 °C, there should remain no contribution in C due to these particular excitations.

To summarize, heat treatment at 840 °C should remove the excitations attributed to Al impurity, and it removed the Schottky excitations sufficiently to allow the temperature dependence and magnitude of C to be measured at temperatures ≤ 0.5 K. In addition, these excitations do not affect the thermal conductivity at $T \leq 0.5$ K. Unfortunately there remain the problems created by heat treatment which must be discussed before the question of TLS excitations can be confronted.

An anneal at 840 °C created an unknown excitation giving a specific heat roughly proportional to $T^{0.5}$ for sample 0 h, and slightly increased a similar contribution already present in sample 3 h. This effect is much reduced, if present at all, in the 27-h sample. The specific heat of the 3-h sample is therefore of no immediate use to our study of glassy behavior.

The thermal conductivity was also reduced in some cases by heat treatment. We find no convincing evidence that this reduction was associated directly with the excitations created by heat treatment. Thus we have discussed the reduction in κ as possibly resulting from the growth of inclusions. To eliminate the phonon scattering caused by the inclusions, one would like to subtract κ^{-1} of the unirradiated crystal from that of the irradiated samples to obtain the additional thermal resistance caused by irradiation. However, the effects of heat treatment depend on the amount of radiation damage. By a comparison of Figs. 3 and 4 it may be seen that the reduction in κ with heat treatment occurs for samples

0 h and 3 h, but not for sample 27 h. Hence subtraction of κ^{-1} of sample 0 h from κ^{-1} of sample 3 h gives the same thermal resistance caused by neutron damage *independent* of whether both samples had been heat treated or both had not been heat treated. However, the presumed growth of inclusions was suppressed in the 27-h sample as evidenced by the lack of a drop in κ upon heat treatment. Thus κ^{-1} of sample 0 h can only be subtracted from κ^{-1} of sample 27 h, both measured prior to heat treatment. In making this calculation for sample 27 h it is to be kept in mind that the additional excitations present before heat treatment, namely the Schottky and Al excitations, did not affect the thermal conductivity below ≈ 0.5 K. The procedure of subtracting κ^{-1} for the 27-h sample also assumes that any TLS excitations which may be present are not altered appreciably by heat treatment. Indeed we have already noted that the thermal resistance of sample 3 h induced by neutron damage did not change with heat treatment. Also, κ of sample 270 h at $T < 0.5$ did not change with heat treatment.

Finally, it is now possible to ask if the irradiated samples show behavior characteristic of a glass. The thermal conductivities are, after subtraction of phonon scattering processes not associated with radiation damage:

$$\begin{aligned} \kappa_{3\text{h}} &= 7.7 \times 10^{-2} T^{2.46}, \\ \kappa_{27\text{h}} &= 9.4 \times 10^{-3} T^{2.13}, \\ \kappa_{270\text{h}} &= 3.3 \times 10^{-4} T^{1.85}, \\ \kappa_{2100\text{h}} &= 4.7 \times 10^{-4} T^{1.87}, \end{aligned} \quad (1)$$

in units of W/cm K and for temperatures ≤ 0.5 K. A T^n temperature dependence below 1 K, with $n \approx 2$, is a characteristic of amorphous materials. These thermal conductivities are next compared with the specific heats of the respective heat-treated samples in the following way.

The tunneling-states model^{2,3} predicts³⁰ $\kappa \propto T^{2-m}$ if the excess specific heat varies as $C \propto T^{1+m}$. These temperature dependencies arise from an energy density $n(E)$ of TLS excitations varying with energy E as $n(E) \propto E^m$. Hence $\kappa \propto T^3 C^{-1}$. To avoid initially the parameters involved in this proportionality, we normalize to the properties of vitreous silica

$$\kappa_c/\kappa_g = C_g/C_c, \quad (2)$$

where g refers to the glassy state (vitreous silica³⁰) and c to the irradiated crystal. In the present paper κ has been measured over a broader range of temperatures than C , and thus C is deduced from Eq. (2). The results are shown as the curves near the respective data in Figs. 6 and 7. The T^3 Debye contribution has been added when plotting these curves. Agreement with the measured specific heats is excellent for the 2100-h and 270-h samples. For the 27-h sample, Eq. (2) predicts a C which is $\approx 10\%$ too small as shown in Fig. 7. For the 3-h sample, the prediction of Eq. (2) is too small by a factor of 20 and falls near line A on Fig. 7. It has already been shown that any TLS excitations would be masked in sample 3 h by unknown excitations created by heat treatment. The results for all irradiated samples are summarized in Table III and will be discussed in greater detail below.

A further comment is required for sample 27 h, which contained a colored central region. The thermal conductivity outside this region was a factor of ≈ 3 larger than inside after phonon scattering processes not associated with neutron irradiation (as deduced from the outer region of 0 h) had been subtracted.²⁷ This would imply a density of TLS excitations a factor of ≈ 3 smaller than in the central region. The final density of TLS excitations produced with neutron damage might therefore be a function of the original "perfection" of the crystal. Also, the specific heat of the central region of sample 27 h should be plotted $\approx 25\%$ higher. This would increase the difference between the measured specific heat and that calculated from κ using Eq. (2) to $\approx 35\%$.

The success achieved in using Eq. (2) indicates that the constant of proportionality between κ^{-1} and C/T^3 is nearly the same for the irradiated samples and is the same as for vitreous silica. The uncertainty ranges from $\approx 10\%$ for the 270 h sample to $\approx 35\%$ for sample 27 h. The constant ratio of $\kappa C/T^3$ in turn implies³¹ that the square of the coupling constant between thermal phonons and TLS excitations is nearly the same for the three samples of disordered crystalline quartz as for vitreous silica, with the coupling constant thus being within $\sim 5\%$ of vitreous silica for sample 270 h and $\approx 18\%$ for sample 27 h. The equivalence of the coupling constants between vitreous silica and a sample of neutron-irradiated crystalline quartz has been demonstrated previously¹⁷ for an ultrasonic frequency of $\approx 10^9$ Hz within an experimental uncertainty of $\approx \pm 30\%$.

To summarize, the thermal conductivity and specific heat below 1 K of 840 °C annealed, neutron-irradiated crystalline α - or β -quartz are indicative of the presence of the same broad spectrum of TLS excitations as found in vitreous silica. The density of such excitations, within the energy interval probed ($0.1 \text{ K} \leq T \leq 1 \text{ K}$), can be as much as a factor of 40 smaller than in vitreous silica. On the other hand, the density of excitations in crystalline quartz can attain 70% of the density found in amorphous, neutron-irradiated vitreous silica.³⁰ Yet this 270-h sample clearly retains a crystalline character as evidenced, for example, by the sharp x-ray reflections mentioned previously.

It is unfortunate that so little is known about neutron damage at the relatively low exposures used here. We have nevertheless made estimates of the amount of radiation damage and the number

TABLE III. Comparison of neutron-irradiated quartz crystals. See text for details of estimates.

Sample \rightarrow	3 h	27 h	270 h	2100 h
(A) radiation-induced clusters per cm^3	8.1×10^{16}	7.6×10^{17}	7.3×10^{18}	5.9×10^{19}
(B) fraction of sample damaged	≈ 0.01	≈ 0.1	≈ 1.0	1.0
(C) total numbers of displaced atoms in damaged volume, per cm^3	8×10^{20}	8×10^{21}	7×10^{22}	(6×10^{23})
(D) ratio of TLS excitation density compared to vitreous silica	(≈ 0.005)	0.024	0.53	0.40
(E) ratio of TLS excitation density compared to neutron irradiated vitreous silica	(≈ 0.007)	0.031	0.69	0.52
(F) total number of TLS excitations of energy $< 1 \text{ K}$, per cm^3	4.3×10^{14}	2.4×10^{15}	5.4×10^{16}	3.9×10^{16}

of localized excitations present. The results are summarized in Table III. In row A of Table III we used the neutron dose in the energy range $0.1 - \infty$ MeV (Table I), an atomic density of 8×10^{22} cm⁻³ and a nuclear cross section³² of 3.5×10^{-24} cm² to obtain the number of "clusters" of displaced atoms. One cluster would be produced by each neutron collision event. If each cluster is assumed³² to include $\approx 10^4$ atoms, row B gives the fraction of the sample damaged and row C gives the total number of displaced atoms. Note that this estimate of damage must saturate between 270 h and 2100 h, i. e., at a dose $> 3 \times 10^{19}$ cm⁻² but $< 2 \times 10^{20}$ cm⁻², where all atoms would be displaced. This does agree with saturation observed in the mass density and other properties³³ near 4×10^{19} cm⁻², and so our estimate may be reasonable. We also note that the increase in magnitude of the Schottky and linear temperature-dependent terms in the specific heat, and the reduction in the thermal conductivity, also saturate and reverse their trend at neutron irradiations between 270 h and 2100 h.

Row D of Table III gives the fraction of TLS excitations relative to the number found in vitreous silica as computed from the ratio of the thermal conductivities at $T \leq 0.5$ K. A ratio for the 3-h sample has been included, although we have no independent evidence for the presence of TLS excitations in this sample. Row E gives the fraction relative to the number found in neutron-irradiated vitreous silica.³⁰ The same fraction, compared with neutron-irradiated vitreous silica which had been heat treated³⁴ (910 °C for 9 h), lies between the values given in rows D and E. Finally, row F gives the total number

of TLS excitations having energies smaller than 1 K. This is a lower limit on the total density. The energy-dependent spectrum certainly extends above 1 K, but how far is not known.

It may be noted from row D (or E) that the fraction of TLS excitations relative to the amorphous state is roughly the same as the fraction of damaged material given by row B. One interpretation might therefore be that the neutrons cause thermal spikes³⁵ resulting in inclusions of amorphous silica. However, the mass densities of the irradiated samples (Table I) are not consistent with such an interpretation. This conclusion has been stated previously.^{17,36} These results suggest that the TLS excitations are not distributed uniformly throughout the irradiated crystal, but rather are arranged within "clusters." The spatial density of TLS excitations within a cluster is roughly the same as in vitreous silica.³⁷

In conclusion, it has been shown that the TLS excitations found in vitreous silica also occur in neutron-damaged crystalline quartz. The properties of the TLS excitations appear to remain unchanged as the total density is reduced by a factor of ≈ 40 . At greater dilution, the TLS excitations are masked by the effect of other excitations created by irradiation or heat treatment.

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