Investigation of Low-Temperature Ultrasonic Absorption in Fast-Neutron Irradiated SiO₂ Glass*

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(Received May 8, 1961)

Ultrasonic attenuation measurements were made in normal and fast-neutron-irradiated fused silica from 7 to 50 Mc/sec and from 1.5° to 200°K. A broad attenuation curve, attributed to a structural relaxation with a distribution of activation energies, occurs at low temperatures. The shape of the loss curve is dependent upon the distribution of activation energies and the amplitude is proportional to the number of structural units which contribute to the relaxation process. Heavy fast-neutron irradiation produced no change in the shape of the curve while the amplitude decreased markedly. A loss associated with a specific defect, an elongated Si−O−Si bond with two equilibrium positions for the bridging oxygen atom, is consistent with the results of this study. The presence of a large number of these defects suggests a new concept of the structure of glass. Evidence is presented to show that thermal spikes, rather than displacement collisions alone, are responsible for the fast-neutron damage in SiO₂.

INTRODUCTION

WHEN either thermally fused silica, i.e., the glassy form of SiO₂, or any of the three crystalline forms of SiO₂ are bombarded by fast neutrons in excess of about 10^{20} neutrons/cm², a single glassy modification results.[1] The physical properties of this neutron disordered silica differ somewhat from those of thermally fused silica. Properties which have been found to change are the density,[2] the low-temperature thermal conductivity,[3] x-ray diffraction,[4,5] refractive index,[6] infrared reflectivity,[5] optical center absorption,[7,8] and electron spin resonance.[8] The present study is concerned with determining the change of another structure sensitive property, the low-temperature anelasticity, as a result of heavy fast-neutron irradiation. A structural relaxation mechanism is suggested which is consistent with the change of attenuation as a function of temperature and frequency and with the change due to fast neutron irradiation. The result of a quantitative study of this mechanism, namely, an elongated Si−O−Si bond with two equilibrium positions for the bridging oxygen atom, suggests a new concept of glass structure. It appears that there are two distinct Si−O−Si bond lengths in equilibrium—one centered about the normal Si−O−Si distance ($\sim$3.2 A) and the other at about 3.8 A. A discussion of two possible mechanisms of fast neutron damage in fused silica leads to the conclusion that thermal spikes are most likely responsible for the irradiation-induced change.

Measurements of the low-temperature ultrasonic attenuation in fused silica have been made by several investigators.[9-12] A comprehensive analysis of the data was made by Anderson and Bömmel,[12] who reported a maximum in the attenuation at a temperature which is dependent upon the frequency of the ultrasonic signal. From the shift of the peak with frequency, an average activation energy of about 1300 cal/mole was calculated. From the broadness of the attenuation curve, it appeared that a multiple relaxation time is involved. That is, the internal friction,

$$1/Q = \sum_i A_i \frac{\omega \tau_i}{1+(\omega \tau_i)^2},$$

where $\tau_i = 1/\omega_i$, $\omega_i = \omega_{0i} e^{-H_i/RT}$, and $A_i =$ the relaxation strength, $\omega =$ the angular frequency of the ultrasonic signal, $\omega_i =$ the relaxation frequency, $\omega_{0i} =$ the characteristic frequency, $\tau_i =$ the relaxation time, $H_i =$ the activation energy, $R =$ the gas constant, and $T =$ the absolute temperature. ω_{0i} was assumed constant for all the processes and the different relaxation frequencies, ω_i, were assumed due to different values of the activation energy. Taking H_i in steps of 100 cal/mole, a distribution of activation energies was calculated.[12] This distribution extended from 0 to 4000 cal/mole with the greatest weight from 0 to 1000 cal/mole. In addition, ω_0 was found to be of the order of 10^{13} cps and the loss mechanism was found to be sensitive to a shear rather than a compressional disturbance. Using this information, the general nature of the loss mechanism was considered by Anderson and Bömmel and they concluded that a structural relaxation was probably responsible for the loss.

In the present study, the following four characteristics of the low temperature attenuation were determined:

1. *The average activation energy and frequency factor of the relaxation process before and after irradiation.* To measure the average activation energy and frequency factor, the shift of the temperature at which the maxi-

[1] M. Wittels and F. A. Sherrill, Phys. Rev. **93**, 1117 (1954).
[2] W. Primak, L. H. Fuchs, and P. Day, J. Am. Ceram. Soc. **38**, 135 (1955).
[3] A. F. Cohen, Oak Ridge National Laboratory Report No. 2413, 1957 (unpublished).
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[5] I. Simon, J. Am. Ceram. Soc. **40**, (1957).
[6] W. Primak, Phys. Rev. **110**, 1240 (1958).
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[8] R. A. Weeks and C. M. Nelson, J. Am. Ceram. Soc. **43**, 389 (1960).

[9] J. W. Marx and J. M. Silvertsen, J. Appl. Phys. **24**, 81 (1953).
[10] H. S. McSkimmin, J. Appl. Phys. **24**, 988 (1953).
[11] M. E. Fine, H. Van Duyne, and N. T. Kenney, J. Appl. Phys. **25**, 402 (1954).
[12] O. L. Anderson and H. E. Bömmel, J. Am. Ceram. Soc. **38**, 125 (1955).

mum attenuation occurs as a function of frequency was determined. This was done at four frequencies from 7.1 to 50 Mc/sec using longitudinal waves.

2. *The irradiation induced change in the relaxation strength and in the distribution of activation energy.* The shape and amplitude of the attenuation curves at 21.5 Mc/sec using shear waves were compared before and after irradiation.

3. *The relative amplitude and shape of shear and longitudinal attenuation curves before and after irradiation.* Since the internal friction, $1/Q$, is the imaginary part of the elastic moduli divided by the real part, then $1/Q=\mu'/\mu$ for shear waves and $(\lambda'+2\mu')/(\lambda+2\mu)$ for longitudinal waves, where λ' and μ' are the imaginary parts of the Lame moduli, λ and μ. By comparing[13] the loss curves due to longitudinal and shear waves, most of the loss was found to be due to the μ' part. If λ' contributes at all, then a distortion of a region containing a relaxing unit by the irradiation could increase the relative effect of the λ' loss.

4. *Recovery of the original level of attenuation by step-annealing the sample.* The heavily irradiated samples are about 2.5%[6] more dense than before irradiation. This density change anneals out gradually as the irradiated sample is heated from room temperature to about 1000°C. A comparative study of the attenuation and density recovery as a function of annealing temperature was made.

FAST NEUTRON DAMAGE IN FUSED SILICA

When fused silica is bombarded by fast neutrons, elastic collisions are the most probable types of interactions since the capture cross section of oxygen and silicon is relatively small at these energies. Such an elastic collision between a neutron and a lattice atom usually results in the displacement of this atom. It is this energetic charged particle which is responsible for the extensive damage caused by the neutron bombardment. Because of the long mean free path of the fast neutrons, this type of irradiation can produce knock-on atoms anywhere within the solid with almost equal probability and consequently can cause homogeneous damaging in a large sample.

An atom which is struck by a neutron travels through the lattice and loses energy both by excitation and ionization of the lattice atoms and by elastic collisions with them. Excitation and ionization are the principal loss mechanisms at energies above a certain region determined by the mass of the bombarding atoms and the lowest excitation energy level of the target atoms. Below this region elastic collisions are the principal means of energy transfer. It is of interest to determine whether, in addition to the displacement of lattice atoms, thermal spikes of sufficiently high temperature

and duration, capable of causing structural changes, can occur as a result of fast-neutron irradiation of fused silica.

A deviation of the properties of thermal spikes in fused silica was made[14] following the general method outlined by Seitz and Koehler[15] and by Dienes and Vineyard.[16] In this computation it was assumed that in order to be capable of causing even a minor structural rearrangement, the spike must have a "temperature" higher than the softening point of SiO$_2$ ($\sim$1600°C) for times greater than a period of lattice atom vibrations ($\sim$10^{-14} to 10^{-13} sec). According to this derivation, small effective thermal spikes ($<$10-A radius) of short duration ($<$10^{-12} sec) could be involved in the fast-neutron damage.

EXPERIMENTAL APPARATUS AND PROCEDURE

An apparatus was assembled to measure ultrasonic attenuation in solids from 1.5° to 373°K and from 5 Mc/sec to 150 Mc/sec. The details of the measuring procedure have been described previously.[17]

A copper sample holder was designed to provide a constant low temperature environment for a solid sample, as shown in Fig. 1. The sample is seated so that most of its bottom surface is a solid-to-gas boundary. It is held in place by a spring-loaded electrode pressing on the bonded quartz crystal transducer on its top surface. Electrical contact is made by the center conductor of the coaxial cable which fits into a hole drilled axially
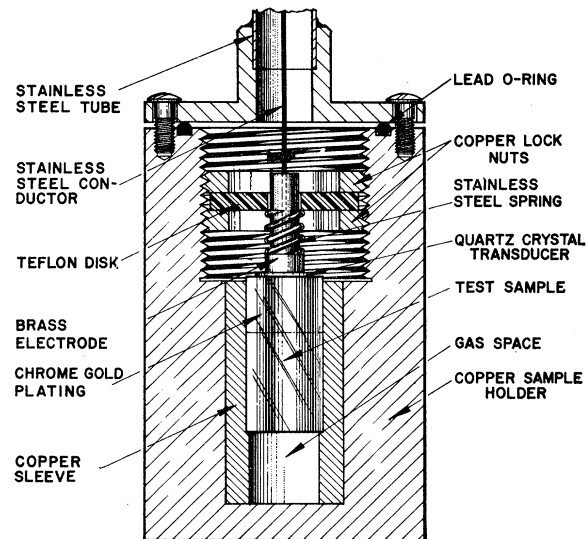

FIG. 1. Diagram of sample holder.

[13] W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Princeton, New Jersey, 1958), pp. 297–298.

[14] R. E. Strakna, Ph.D. thesis, University of Connecticut, 1960 (unpublished).

[15] F. Seitz and J. S. Koehler, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, pp. 305–448.

[16] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

[17] See reference 13, Chapter 4.

in the electrode. This provides a nonrigid connection
between the sample holder and this conductor which is
helpful in assembling the unit. The holder is vacuum
sealed by means of a lead O-ring seated in a groove in
the holder. These O-rings were punched out of $\frac{1}{16}$-in.
lead sheets.

Two fused silica samples were used in this work. Both
were Amersil optical grade which had been polished flat
to within $\frac{1}{5}$ wavelength of sodium light and parallel to
within 5 sec of arc. One end of each sample was chrome-
gold plated to serve as one of the transducer electrodes.
Irradiated sample No. 2 was the one used by Anderson
and Bömmel in their work on unirradiated silica using
shear waves at 20 Mc/sec. Most of the runs on irradiated
silica were made on this sample which had been exposed
to fast-neutron irradiation in the Chalk River facility,
at an integrated flux density apparently in excess of
10^{19} neutrons/cm². This was indicated by a saturation
density of about 2.26 g/cm³. The attenuation measure-
ments in this sample were taken about four years after
irradiation. Sample No. 1 was exposed to fast-neutron
bombardment in excess of 5×10^{19} neutrons/cm² at the
Oak Ridge National Laboratory and a measurement was
taken about one year after exposure. These samples had
to be resurfaced after irradiation, since the irradiation
somewhat distorted the surface. For example, in sample
No. 1 the parallelism was off by more than one minute
of arc as compared to less than five seconds before
irradiation. During the annealing studies, sample No. 2
had to be resurfaced because the surface parallelism and
flatness were affected as it reverted to normal fused
silica.

A 7-Mc X-cut longitudinal or an AC-cut shear crystal-
line quartz transducer was bonded to the specimen with
a thin layer of DC-200 series, 1000 centistoke silicone
oil. A surface roughness of about 10 microinches was
used on both the sample and transducer. Excellent
exponential echo decay patterns were obtained using the
following simple transducer-mounting technique. A
small drop of silicone oil was spread on the sample sur-
face and the transducer placed upon it. The flat spring
loaded electrode was then placed on top, spreading the
bonding agent uniformly between the two surfaces. The
best bonding occurred by quickly cooling the sample
(several minutes) from room temperature to liquid
nitrogen temperature. Temperatures from 77° to 45°K
were attained by pumping on liquid and solid nitrogen.
For lower temperatures liquid helium was used. The
warm-up time of the sample holder was long enough so
that, effectively, thermal equilibrium was established
at any intermediate temperature between helium and
nitrogen.

It is possible to measure the absolute attenuation in
fused silica in the lower megacycle frequency range be-
cause an accurate background loss determination can be
made. The attenuation near room temperature is so low
that the entire loss measured at that temperature is the
background loss. An attenuation range of from 30 to
60 db is utilized in this study with a probable error of
about ±1.5 db (5%—2.5%). Both the velocity and
frequency of the signal easily can be measured to better
than 0.5% so that the accuracy of the determination of
the value of $1/Q$ at any temperature is determined pri-
marily by the accuracy of the attenuation measurement.

RESULTS

Longitudinal attenuation measurements were made in
unirradiated sample No. 1 at 7.1, 21.5, 35.8, and 50.0
Mc/sec and in irradiated sample No. 2 at 21.5, 35.8, and
50.0 Mc/sec. Using the relationship $1/Q = Av/\pi f$, where
$A =$ the attenuation in nepers/cm, $v =$ the velocity (as-
sumed constant in these computations), and $f =$ the
frequency, the internal friction curves of Fig. 2 were
plotted. The justification for comparing data from two
different samples is derived from the good agreement
between the attenuation in samples 1 and 2 before
irradiation as seen in Fig. 4.

Figure 3 is a plot of the logarithm of the frequency
vs the reciprocal of the temperature at which the maxi-
mum attenuation occurs for longitudinal waves in
sample No. 1. A line drawn through these points and
two others approximated from the low-frequency study
of Fine et al.,[11] satisfies the rate equation shown on the
diagram. Here ω is the relaxation frequency correspond-
ing to the temperature T, ω_0 is the characteristic fre-
quency of the process found by the intercept of this
curve with the vertical axis, and H is the average activa-
tion energy, determined from the slope. The values of H
and ω_0 are essentially the same as found in the earlier
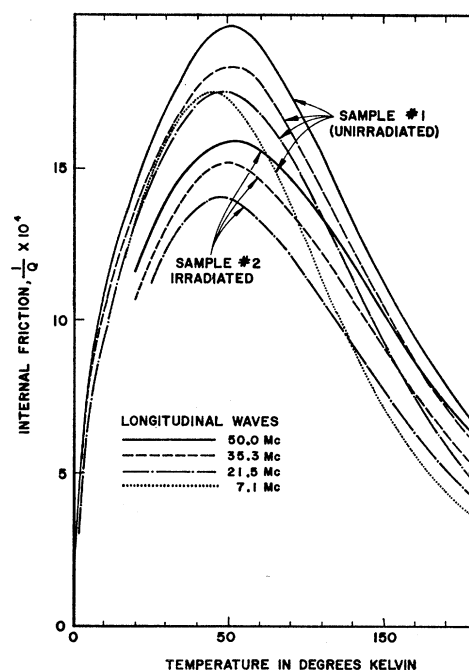

FIG. 2. Internal friction with longitudinal waves in unirradiated
sample No. 1 and irradiated sample No. 2.

study.[12] As seen in Fig. 2, there is no detectable change in the temperature at which the maximum at each frequency occurs, so that ω_0 and H_{av} have not changed as a result of the irradiation.

In Fig. 4 a comparison of the internal friction before and after irradiation of both samples 1 and 2 is made using shear waves. If the attenuation curve of sample 2 is multiplied by a constant, it is found that its shape is the same as that taken before irradiation. Also, the attenuation of sample 1 shows no marked deviation from this shape as seen from curve (d) multiplied by a factor of 4. Since both of the samples were irradiated close to a saturation density, it appears that whatever damaging process is responsible for the decrease in attenuation continues after the density has reached a constant value.

By comparing the 21.5-Mc/sec attenuation curves in Figs. 2 and 4, it can be seen that the irradiation has no detectable effect upon the relative amplitude of the attenuation of the longitudinal and shear waves.

Figure 5 shows the recovery of the internal friction in sample 2 by step annealing at several temperatures. The sample was heated to the indicated temperature, held at this temperature for one-half hour, and then slowly cooled to room temperature. Also, a comparison was made of the recovery of the density including data from Primak's[6] study where the annealing procedure was similar to that used here. As seen in this figure, the density recovers at a lower temperature than the attenuation. At 980°C the density has completely recovered while the attenuation has recovered only about 45% of its original value. After heating at 1150°C for one-half
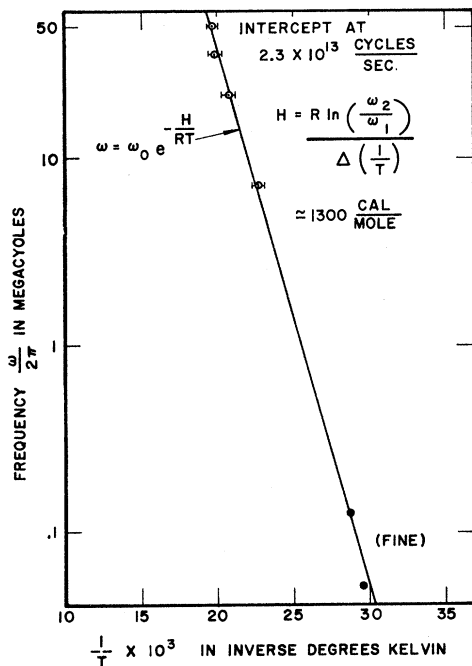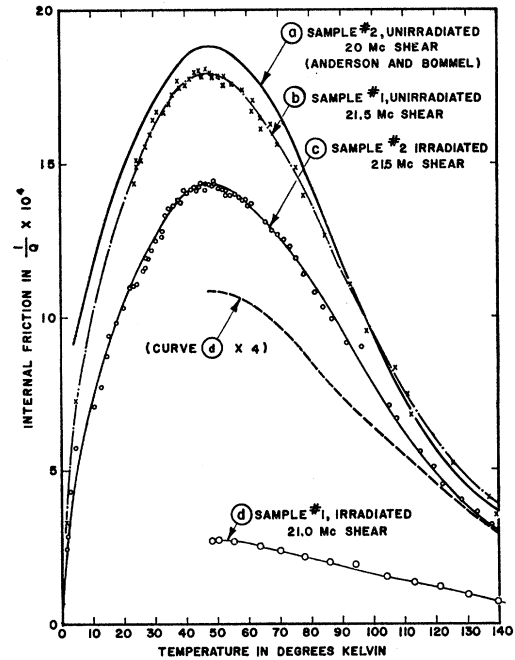
FIG. 4. Comparison of internal friction before and after irradiation in samples 1 and 2 using shear waves.

hour, the attenuation has just about completely recovered.

The following is a summary of the results of and implications drawn from the attenuation measurements. The first three statements were initially reported and

FIG. 3. Plot of $\ln f$ vs $1/T$ for longitudinal waves in sample No. 1.
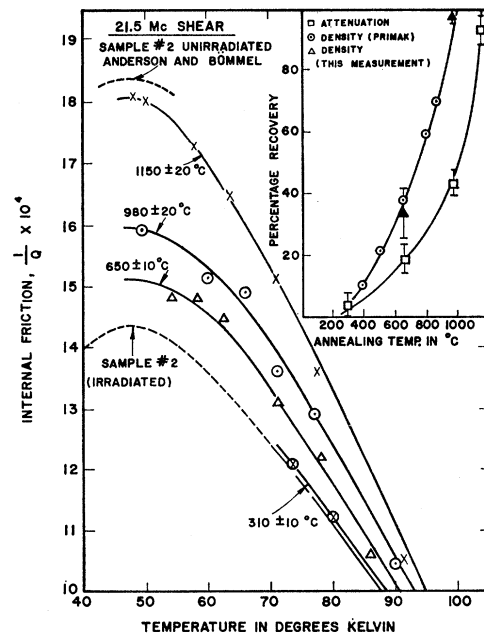
FIG. 5. Recovery of attenuation and density in sample No. 2 with annealing at 310°, 650°, 980°, and 1150°C for $\frac{1}{2}$ hour.

discussed in reference 12, while the last four were derived from the present study.

1. An atomic rearrangement mechanism is indicated by the frequency factor of about 10^{13} cps.

2. There is a distribution of activation energies (0 to about 4000 cal/mole) with the highest density at the lower energies in normal fused silica.

3. The relaxation mechanism is much more sensitive to a shear disturbance than to a compressional one.

4. The distribution of activation energy is unchanged by the fast neutron irradiation.

5. The relaxation strength is decreased by the irradiation (about 20% in sample 2 and 80% in sample 1).

6. The relative amplitude of the shear and longitudinal attenuation is unchanged by the irradiation.

7. The temperature dependence of the recovery of the original density differs from that of the attenuation.

DISCUSSION

A relaxation process with a high-frequency factor ($\sim 10^{13}$ sec^{-1}) and a low-activation energy (~ 0.05 ev) was found from the attenuation measurements. This high-frequency factor excludes the possibility of a large section of the structure relaxing. The shifting of an atom between equilibrium positions separated by a small potential barrier is indicated. Such a relaxation mechanism was suggested by Anderson and Bömmel[12] who base their analysis on the Zachariasen-Warren random model of glass where the silicon-oxygen tetrahedra are assumed to be bonded to each other with a common oxygen lying in a straight line between the silicon atoms.
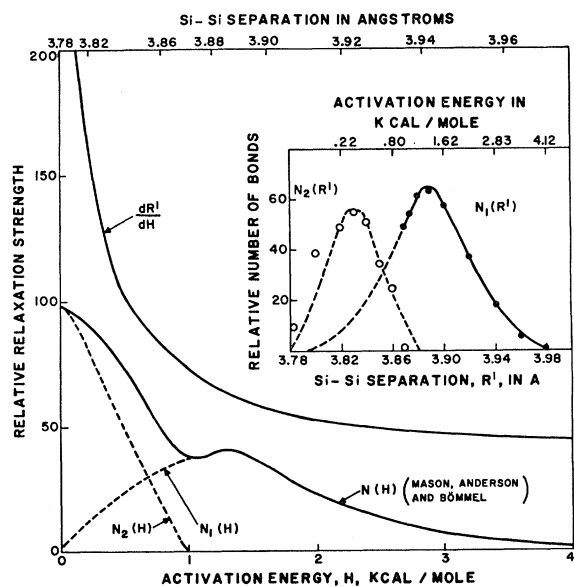

FIG. 6. Relative distribution of activation energies (corresponding Si—O—Si bond lengths derived from model are given at top of figure). The insert shows the relative distribution of elongated Si—O—Si bond lengths. Solid circles are derived from $N(H)/(dR'/dH)$. Open circles are derived from $N_2(H)/(dR'/dH)$.

They assumed that while most of the Si—O—Si bonds are straight, some deviate slightly from 180°. These slightly displaced oxygen atoms can assume positions of almost equal energy on opposite sides of the Si—O—Si bonds. The stress due to the ultrasonic signal biases one position with respect to the other and alters the distribution of atoms. If the period of the signal is comparable to the relaxation time of the readjustment to the equilibrium distribution, the signal is attenuated. The distribution of bond angles was assumed to be responsible for the distribution of activation energy of the mechanism.

Since, in the present study, no detectable change in the activation energy with irradiation occurs while the relaxation strength decreases, the damaging mechanism appears either to eliminate a relaxing unit or leave it unchanged. This irradiation damage of the silica structure may occur in two ways—by thermal spikes or by displacement collisions. If thermal spikes are responsible, the structure may become compacted due to the heating and rearrangement of many small regions. If the damage occurs only by displacement collisions, resulting in interstitials and vacancies, the structure must be strongly affected since a significant compacting does occur. In either type of damage, a change in the relative orientation of many tetrahedra seems likely. An interpretation given by Weeks and Nelson[18] of their electron spin resonance studies of fused silica before and after heavy fast irradiation indicates a distortion of the structure. These authors found that α quartz and fused silica appear to have a similar short-range order which, upon irradiation, is markedly changed. If such a distortion of the structure does occur, it is difficult to explain the absence of a change in the distribution of activation energy consistent with a mechanism connected to a slight distortion of the structure.

From the good agreement in the amplitude of the attenuation curves of the different samples as seen, for example, in Fig. 4, impurities do not seem to be a deter-

TABLE I. Activation energy and anomalous Si—O distances as a function of Si—Si separation.

R' in A	R(Si—O)$_1$ in A	R(Si—O)$_2$ in A	H in cal/mole
3.76	1.88	1.88	0
3.78	1.89	1.89	0
3.80	1.82	1.98	69
3.82	1.78	2.06	245
3.84	1.76	2.08	467
3.86	1.74	2.12	798
3.88	1.73	2.15	1200
3.90	1.72	2.18	1680
3.92	1.72	2.20	2220
3.94	1.70	2.24	2820
3.96	1.69	2.27	3480
3.98	1.70	2.28	4150
4.00	1.68	2.32	4930
4.02	1.68	2.34	5730

[18] R. A. Weeks and C. M. Nelson, Oak Ridge National Laboratory Report 2829, 1959 (unpublished), pp. 162–165.
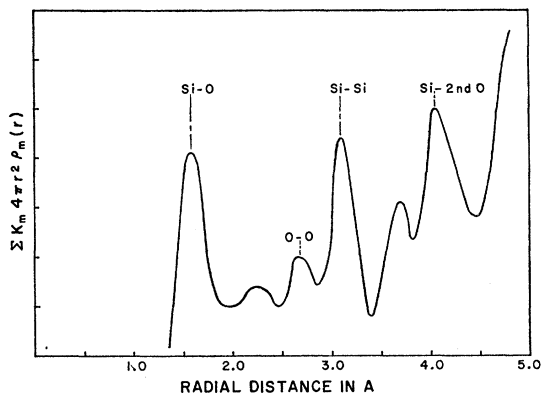
FIG. 7. X-ray electron density distribution of SiO₂ as a function of radial distance from a given atom. (Curve was redrawn from Fig. 1 of reference 22.)
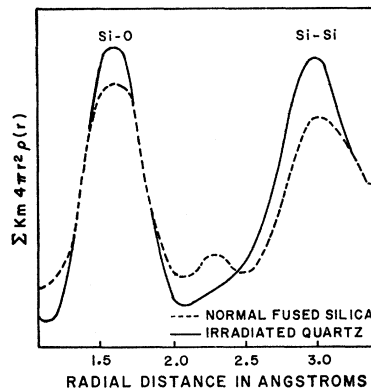

FIG. 8. X-ray electron density distribution of fused silica and irradiated quartz as a function of radial distance from a given atom. (Curve was redrawn from Fig. 3 of reference 5.)

mining factor in the attenuation. That is, if the attenuation were due to an impurity, the amplitude of the attenuation curve would be dependent upon the impurity concentration; this has not been observed.

Since neither a slight distortion of the structure nor impurity defects appear to be responsible for the loss, a nonimpurity defect may be involved. Possible non-impurity defects in glassy SiO₂ are (1) free oxygen interstitials, (2) nonbridging oxygen ions, (3) free silicon interstitials, (4) oxygen vacancies, (5) silicon vacancies, (6) an association of two nonbridging oxygens (designated as a Q center by Kats and Stevels)[19] and (7) an increased Si—Si distance resulting in a nonbridging oxygen and an unsaturated silicon. It will be shown that a loss mechanism associated with the elongated Si—O—Si bond with two equilibrium positions for the bridging oxygen atom is consistent with the results of this study.

For sufficiently large values of Si—Si separation, the single energy minimum for the bridging oxygen atom is replaced by two equilibrium positions. The relaxation time of the loss mechanism is dependent upon the barrier height between alternate oxygen positions. A calculation of this barrier height as a function of Si—Si separation was made. The interaction of the bridging oxygen atom with the two silicons is represented by the sum of two Morse potentials where the potential energy of the oxygen atom at position R from a silicon atom is given by

$$U_{R'}(R) = U_0 [e^{-4.8(R-R_0)} - 2e^{-2.4(R-R_0)}$$
$$+ e^{-4.8(R'-R-R_0)} - 2e^{-2.4(R'-R-R_0)}],$$

where U_0 is the Si—O bond energy ($\sim 9 \times 10^4$ cal/mole), R_0 is the normal Si—O distance (~ 1.6 A), and R' is the Si—Si distance. The resulting activation energy and "anomalous" Si—O bond distances as a function of Si—Si separation are listed in Table I.

The relaxation strength of a given range of activation energies, ΔH, is proportional to the number of Si—O—Si

bonds having an energy barrier in this range. Assuming an equal probability for all Si—Si separations, the relative number of bonds per unit H, dR'/dH, was calculated. The relative distribution of activation energies, $N(H)$ (calculated by Mason[20] from the attenuation study of Anderson and Bömmel[12]) should be equal to dR'/dH multiplied by the actual Si—Si spatial distribution function, $N(R')$. By separating the distribution of activation energies, $N(H)$, into two parts designated by $N_1(H)$ and $N_2(H)$ in Fig. 6, a strikingly symmetrical spatial distribution function, $N_1(R')$ with a maximum at 3.89 A (~ 1300 cal/mole) is found corresponding to $N_1(H)$. See insert in Fig. 6. Points corresponding to $N_2(H)$ are also plotted on the spatial distribution diagram and these strongly indicate a second symmetrical peak at 3.83 A (~ 300 cal/mole). In this calculation no parameters were adjusted to obtain this distribution. The only available adjustable parameter is the constant in the exponential of the Morse potential and this was assigned the value 2.4 A⁻¹ based on an average value of the constant calculated for a number of diatomic molecules.[21]

According to the relationship listed in Table I, an Si—Si separation centered at about 3.86 A will result in two "anomalous" Si—O distances—one peaked at 1.74 A and the other at 2.12 A. If this defect occurs in at least a few percent of the total number of Si—O—Si bonds, then an x-ray radial distribution curve with sufficient resolution should show peaks at 3.86, 1.74, and 2.12 A. Figure 7 shows an x-ray radial distribution curve of SiO₂ taken from a study by Richter et al.[22] Notice that peaks appear approximately where predicted in Table I with the exception of the 1.74-A peak which apparently isn't resolved from the large normal Si—O peak at 1.6 A. In Fig. 8, which is part of a radial distribution curve reported by Simon[5] in a comparative

[19] A. Kats and J. M. Stevels, Philips Research Repts. 11, 115 (1956).

[20] See reference 13, p. 301.
[21] E. A. Moelwyn-Hughes, Physical Chemistry (Pergamon Press, New York, 1957), p. 306.
[22] H. Richter, G. Breitlung, and F. Herre, Naturwissenschaften 40, 621 (1953).

study of fast neutron irradiated quartz and normal fused silica, the change with irradiation is as expected from the attenuation study and the elongated bond model. The anomalous Si—O peak (at 2.25 A) in the unirradiated sample decreases with irradiation with a corresponding gain in the normal Si—O peak. Also the Si—Si peak increases as expected.

An estimation of the relative population of anomalous to normal Si—O—Si bonds can be found by comparing the areas of the respective peaks on the x-ray distribution curve of Fig. 6. According to this comparison, an exceptionally large proportion, 20% to 30% of the total number of Si—O—Si bonds, are elongated.

The ratio of elongated bonds to normal bonds in thermally fused silica is characteristic of the equilibrium concentration of these bonds at the annealing temperature. The attenuation study indicates that this ratio decreases with irradiation. A consistent explanation of the change is that a metastable structure, characteristic of a high temperature and probably an increased pressure, is quenched in during the very rapid cooling of thermal spikes. The frozen-in structure is thermally unstable and anneals out gradually from about 300° to 1150°C, the normal annealing temperature. An alternate explanation of the decrease of contributing units with irradiation is that bridging oxygen atoms are knocked into interstitial positions. However, this is not consistent with the findings of this study for several reasons. First, according to Fig. 8, the irradiation causes a decrease in the number of elongated Si—O bonds with a comparable increase in the number of normal Si—O bonds. Secondly, if the percentage of elongated bonds is as large as estimated from Fig. 7, then the vacancies created by displacing the oxygen atoms would be traps for other knock-on oxygens, thus making it unreasonable to expect an 80% decrease in elongated bonds. Also, the densification of silica follows naturally from a decrease of the relative number of elongated bonds while it is difficult to explain on the basis of a rearrangement resulting from an increase in point defects alone. On the basis of these arguments, it appears that thermal spikes, resulting in small superheated regions which are rapidly quenched in, cause metastable regions in which the ratio of elongated to normal Si—O—Si bonds is decreased.

The low-temperature relaxation loss in other silicates is very likely caused by the same mechanism as in fused silica. In Fig. 10.13 of reference 13, the distribution of activation energies of the loss mechanism in synthetic quartz is given. Using the method utilized here for determining the spatial distribution of bond lengths

corresponding to the distribution of activation energies, a symmetrical distribution with a half width of 0.01 A (compared to 0.1 A in fused silica) is found at about 1300 cal/mole while the 300-cal/mole peak is absent. Also, the very small 1300-cal/mole peak found in natural crystalline quartz would result in a very narrow spatial distribution since it closely represents a loss with a single relaxation time.

SUMMARY

Heavy fast-neutron irradiation of fused silica decreases the relaxation strength of the low-temperature loss mechanism but does not affect the distribution of activation energies. A specific defect relaxation mechanism, the elongated Si—O—Si bond with two potential minima for the bridging oxygen atom is consistent with the results of this study. A model of glass structure with two distinct and widely separated Si—O—Si distances (or their equivalent in other glasses) is indicated. The mechanism of fast-neutron damage in fused silica appears to be a rearrangement due to thermal spikes rather than simply the result of many displacement collisions.

Note added in proof. X-ray diffraction studies on amorphous solids are influenced by diffraction errors which can result in false subsidiary peaks in the radial electron density curves. Consequently, the possibility of coincidental agreement of the predicted peaks and those found in Fig. 7 as well as in the variation of peak heights in Fig. 8 should be mentioned. In any event, the defect model is derived solely on the basis of the ultrasonic studies and reference to the x-ray work is important only in that it permits one to roughly estimate the relative number of extended to normal Si-O-Si bands. An independent means of determining this ratio is needed in order to resolve this point satisfactorily.

ACKNOWLEDGMENTS