Spin Relaxation of Atomic Hydrogen in Fused Silica: Temperature Dependence*

D. W. Feldman, J. G. Castle, Jr., and G. R. Wagner

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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An unusual temperature dependence has been found for the spin-lattice relaxation time T_1 of the hydrogen atoms trapped in fused silica; $1/T_1$ is found to vary strongly with temperature in the range between 2 and 20°K and to approach proportionality to T above 20°K. After removal of some of the hydrogen centers by thermal annealing, the relaxation is slower but has essentially the same temperature dependence. The data are interpreted in terms of a localized resonance mode of vibration having a large temperature-independent amplitude in the neighborhood of the hydrogen spin. The model proposed by Murphy fits the data accurately over four decades in T_1 with a characteristic frequency of 2.8 (10^{11}) cps.

INTRODUCTION

ATOMIC hydrogen has been observed[1] as an interstitial impurity in some crystals. The motion of the hydrogen atom in these cases is expected to include high-frequency local modes. The frequency of the local modes has been determined[2] for the case of hydrogen in CaF_2 from measurements of spin-lattice relaxation.

Atomic hydrogen is stable at low temperatures in SiO_2 crystals[3] and in SiO_2 glass.[4] In each case the ESR spectra give $g=2.002$ and a hyperfine coupling nearly that of the free atom. The observed hyperfine coupling to silicon nuclei indicates that the site in crystalline SiO_2 differs from the site in CaF_2 in that it appears to involve hydrogen as an interstitial near a vacancy, possibly a complex vacancy. Details of the defect structure are not yet clear, but the hyperfine values indicate that the sites for the hydrogen atom in the fused silica are similar to the sites in the crystalline SiO_2, but have a larger volume. Masses associated with vacancies in SiO_2 have been found[5,6] to move with large amplitudes for at least some of the low-frequency modes. The frequencies of these characteristic motions were found to be very similar in crystalline and glass samples, the lowest ones corresponding to temperatures of about 20°K in each case. Thus spin relaxation of atomic hydrogen in SiO_2 is expected to involve large amplitudes in low-frequency modes as well as in local modes.

It is the purpose of this paper to present spin-relaxation measurements for atomic hydrogen in fused silica and to interpret them in terms of novel relaxation mechanisms presented by Murphy in the following paper.[7]

EXPERIMENTAL DETAILS

The sample used was a piece of u.v. grade, fused silica from Corning's #7940 series. A concentration of about 3×10^{18} cm^{-3} atomic hydrogen centers was produced by subjecting the sample to a dose of about 10^7 R of 0.5-MeV gamma rays at liquid-nitrogen temperature. The sample was then mounted in a specially designed microwave cavity while under liquid nitrogen, so that at no time was the sample temperature greater than 80°K before the first relaxation measurements were made.

Relaxation times were measured using the field-sweep, inversion-recovery technique described elsewhere.[8] Thermocouples were used to measure the sample temperature above 4.2°K, and helium-vapor-pressure measurements were used at and below 4.2°K.

The first data were taken about one day after the end of the irradiation and are indicated by o in Fig. 1. The sample then was kept at 80°K for a week and the data indicated by △ taken. The data marked by ● were taken after further annealing the sample at 102°K for an hour, and the data marked by ▽ and ▲ were taken after annealing the sample for a few minutes at 112 and 115°K, respectively.

The concentration of hydrogen centers after each successive anneal was determined by comparing the resonance-signal intensity to that from a piece of MgO containing a known amount of Cr^{3+}.

RESULTS

After each anneal, the resulting density of hydrogen centers was found to be stable at all temperatures up to and including the annealing temperature. The densities are given in Fig. 1. The relative densities have an accuracy of about $\pm 20\%$; the absolute density, $\approx \pm 50\%$.

Figure 1 shows the temperature dependence of the relaxation time τ for the lower field component of the atomic-hydrogen doublet at 9 Gc/sec. A single relaxation time for the hydrogen system was found in each recovery. The data display some characteristics common to each density: above 20°K $1/\tau$ varies approximately

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[4] Reference 3 and references therein.

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[6] J. G. Castle, Jr., and D. W. Feldman, J. Appl. Phys. **36**, 124 (1965).

[7] J. Murphy, following paper, Phys. Rev. **145**, 241 (1966).

[8] J. G. Castle, Jr., D. W. Feldman, P. G. Klemens, and R. A. Weeks, Phys. Rev. **130**, 577 (1963).

as T; between 2 and 20°K the temperature dependence of $1/\tau$ is significantly stronger than T; below 2°K the relaxation time varies slowly with temperature. At any temperature the relaxation time shows an increase with decreasing density.

The temperature dependence predicted for any of the normal Raman processes is inconsistent with the data

in Fig. 1. The set of data taken after the anneal at 102°K and shown in Fig. 1 by ● is accurately described, using one of Murphy's functions,[7] by

$$1/\tau = AT + BM_1(\theta/T), \qquad (1)$$

where $A = 0.030 \pm 0.003$ sec^{-1}°K^{-1}, $B = 14 \pm 2$ sec^{-1}, and

$$M_1(\theta/T) = \frac{\sum_{i=1}^{\infty} (2i+1)[1-(2i+1)^{-2}]^2 \exp[-i^2\theta/T][\exp[(2i+1)\theta/T]-1]^{-1}}{\sum_{i=1}^{\infty} \exp[-i^2\theta/T]} \qquad (2)$$

with $3\theta = 13.5 \pm 1.5$°K. Equation (2) has only the $l=0$ terms of Eq. (16) Ref. 7; the others add less than 0.1% to M_1. The other sets of data are described by Eq. (1) with the following parameters:

for △, $A = 0.08$ sec^{-1} °K^{-1}, $B = 75 \pm 15$ sec^{-1},

and $3\theta = 15.6 \pm 1.5$°K;

for ▽, $A = 0.015$ sec^{-1} °K^{-1}, $B = 3.2 \pm 0.4$ sec^{-1},

and $3\theta = 13.0 \pm 1.5$°K.

The data may also be described by[7]

$$1/\tau = AT + BG(\theta/T)z \qquad (3)$$

where for the points labeled by ●, $A = 0.030 \pm 0.003$ sec^{-1} °K^{-1}, $B = 33 \pm 3$ sec^{-1}, and $G = \text{csch}(\theta/T)$ with $\theta = 16 \pm 1$°K. It should be noted that in both the expressions of (1) and (3) the term, AT, can be replaced by a constant term without altering the agreement.

To investigate the homogeneity of the resonance, a section of the line was inverted and the recovery monitored. The initial width of the inverted "hole" was about 20% of the 0.65 Oe half-power width of the line. The time for this hole to "heal"[9] was of the order of 1 sec when the density was 1.6×10^{18} cm^{-3} and τ was 22 sec.

Other resonances were observed with g values near 2.0. After the anneal at 115°K, a resonance with a full width at half-power of about 50 Oe and corresponding to a spin density many times that of the hydrogen centers was observed to have $\tau \approx 0.1$ sec at 1.5°K. A resonance with a width of about 1 Oe sat atop the wide line near its peak and had a relaxation time of about 25 sec at 1.5°K. No observation of these resonances was attempted before the 115°K anneal.

DISCUSSION

The observed temperature dependence of spin relaxation of atomic hydrogen in silica is unusual and cannot be accounted for by any of the heretofore published

descriptions.[10] The proportionality with T, observed above 20°K and shown in Fig. 1, cannot be due to a "direct" or one-phonon relaxation process because a stronger variation with T is observed below 20°K. Relaxation via Raman processes involves the simultaneous interaction of two modes of vibration of the lattice for each spin flip. Normally, the motion in each of the two modes is described accurately as being harmonic because the local strain is very small. Such Raman processes have a strong temperature dependence at very low temperatures, dominate the relaxation at higher temperatures, but give T^2 dependence at the highest temperatures where the mean-square amplitude in each of the two modes is then proportional to T. Therefore, such Raman processes cannot give rise to the observed proportionality to T above 20°K.

The resonant Raman processes analyzed by Orbach[10] would have the temperature dependence given by

$$1/T_{1R} = C[\exp(\Delta/kT)-1]^{-1}, \qquad (4)$$

where Δ is the energy of an excited electronic state of the center. This temperature dependence also obtains if the excited state is a vibrational state having a different g value than the ground state. Equation (4) fits the data in Fig. 1 rather well with $\Delta/k = 14$°K. However, the atomic hydrogen center is not expected to have any low-lying electronic states or vibrational states with a different g value than the ground state, so this agreement with the data of Fig. 1 is not considered significant.

Relaxation of atomic hydrogen in silica above 2°K can be explained by a Raman process in which one of the two modes involved in each spin flip has a temperature-independent amplitude. Then the transition probability, $1/T_1$, would vary with the mean square amplitude in the other mode of vibration, and this would give proportionality to T in the limit of high temperatures. So one needs a structural model having a mode of motion which plays a role in flipping the

[9] R. W. Warren, D. W. Feldman, and J. G. Castle, Jr., Phys. Rev. **136**, A1347 (1964).

[10] See, for example, R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

hydrogen spin but which has a temperature-independent amplitude.

There are probably several structural models for the relaxation which would lead to this kind of motion. Two such models are discussed by Murphy.[7] One involves the motion of the hydrogen trapped in a deep square well and the other considers the hydrogen center to have two (or more) stable configurations between which it may tunnel. In each of these models, the source of the polarization of the hydrogen atom is located a short distance away. The source may be, for example, an ion interacting with the hydrogen via an electric field or a magnetic dipole coupling to the spin directly. The distance to the source appears as a factor in the coefficient of the spin relaxation time for each model, while the temperature dependence is determined by the energies of motion which are presumed to be independent of this distance.

The Raman relaxation function predicted by Murphy[7] for the deep-square-well model is given in Eq. (2). The best fit of this two-parameter function to the data for one hydrogen density is plotted as the solid curve in Fig. 1, and is an excellent fit with no systematic deviations for $T > 3°$K. The dashed curve is the asymptotic limit of the solid curve. The other sets of relaxation data are well fitted by Eq. (2) with different coefficients but essentially the same temperature dependence, indicated by the same value of θ. It is noted[7] that if the spin flip of the hydrogen atom is produced by the electric field from an interstitial ion, then either that ion or the hydrogen atom can be in the deep well, but the well dimensions would vary accordingly. For example, if the hydrogen centers have H⁰ in a deep well, then the first energy gap of $3\theta = 14°$K would mean that in one dimension the steep sides of the well are about 7 Å apart and in the other dimensions, much closer.

The expression for the temperature dependence of spin relaxation via tunneling between two equivalent positions is given as $G(\theta/T)$ in Eq. (3). This function gives a fit to the data which is acceptable, but inferior to that of the deep well. However, the fit may be made better by using three or more parameters derived, for example, on a model in which the tunneling has a distribution of characteristic frequencies for the hydrogen centers due to slight variations in their surroundings. It should be noted that the energy gap of 14°K for the deep square well agrees with the 16°K value found for tunneling.

Simplicity gives preference to the two-parameter, deep-well model in which every hydrogen center in the silica has closely the same major dimension for its well. For either model, variation in the coefficient B, but not in the temperature dependence, will be caused by a variation in the distance between the hydrogen atom and the source of coupling.

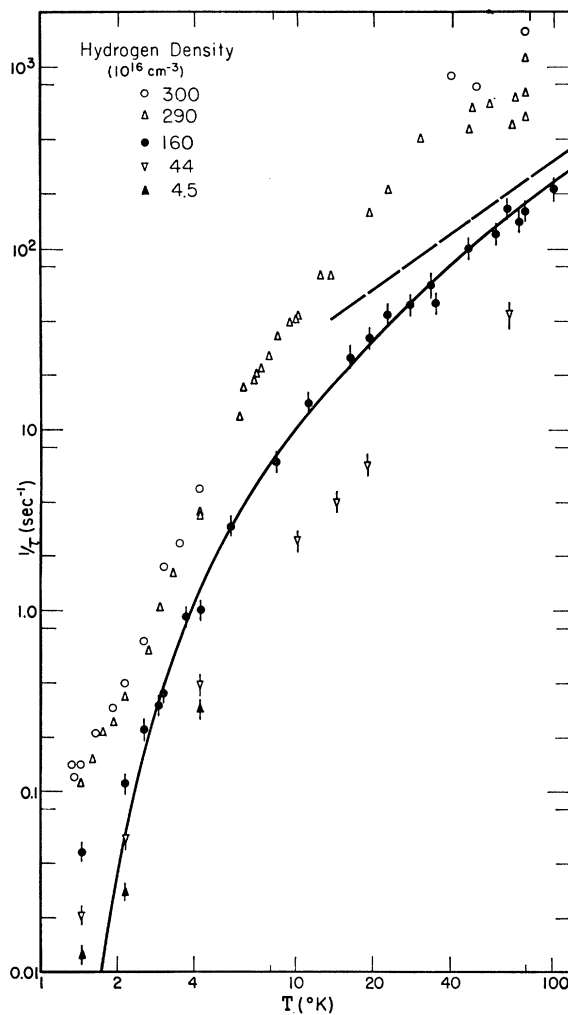These models are also consistent with the observed

Fig. 1. Reciprocal of relaxation time versus temperature for atomic hydrogen in fused silica at 9 Gc/sec. Both scales are logarithmic. The various symbols represent relaxation times measured at the densities indicated. The theoretical curves shown are discussed in the text.

hole healing, exponential recoveries, and effects of annealing. This can be seen from the following discussion: Annealing to a lower density reduces the relaxation of the entire hydrogen spin system somehow without significantly changing its temperature dependence. A "hole" in the spin-resonance line heals much more slowly than the spins relax to the lattice over most of the temperature range in Fig. 1. The recoveries of equilibrium after inversion of the whole line occur with a single time constant in each case. Thus every hydrogen center has the same T_1 after a given anneal or some of the hydrogen centers in each part of the observed inhomogeneous line have a shorter T_1 and control[9] the relaxation of the entire system. If the former were the case, then annealing would change the structure of

every hydrogen center in the same way. If the latter obtains, then annealing destroys progressively those hydrogen centers with the shorter T_1's. This is reasonable if the centers in the initial hydrogen system had a distribution of T_1's corresponding to a distribution of some parameter like the distance between the hydrogen atom and its source of coupling and if annealing destroys preferentially those centers with the shorter distances.

The distribution of distances, if indeed that is the appropriate parameter, may involve a discrete set of values for the distance. A more extensive comparison between hydrogen density and relaxation time would be required to ascertain whether the increments observed in the relaxation are significant. It should be noted that the last decrease in density shown in Fig. 1 produced a smaller change in T_1 than the previous, less drastic reductions in density, and that the temperature dependence for the lowest density is not well defined.

One final comment on cross relaxation is in order. A 25-sec relaxation time for the narrow line (probably due to E' centers) atop the broad one at $g=2.00$ was observed for the conditions in which the broad one had a τ of only 100 msec. Since cross relaxation from this broad line to the hydrogen lines will be slower than to the E' line (due to less overlap between them), this cross relaxation did not affect our observed values of the relaxation time for the hydrogen centers. No other resonances were observed, so we have indicated that the relaxation below 2.1°K is due to the direct process, but this interpretation of the data below 2.1°K remains tentative.

It is interesting to note that previously published[5,6] data on relaxation of E' centers in both crystalline SiO_2 and silica glass may also be explained on the basis of the models discussed here. Describing the lowest temperature Raman relaxation observed for E' centers by expression (2) gives $3\theta_1=23\pm2°K$ in crystalline SiO_2 and $3\theta_1=25\pm2°K$ in the glass. These values for the vibrational energies are significantly higher than that for H^0 centers.

COMPARISON TO OTHER PROPERTIES OF SILICA

The results of measurements of specific heat[11] and ultrasonic attenuation[12] in fused silica have been interpreted in terms of excess motion of some of the atoms at low frequencies. Flubacher et al.[11] find excess specific heat at low temperatures for which the simplest explanation is excitation for about 10^{-4} of the molecules at three frequencies corresponding to the energies of about 13, 38, and 60°K. The square-well model[7] which describes the spin relaxation of the atomic hydrogen centers gives a similar excitation spectrum but quantitative agreement with the excess specific heat is not obtained. A similar correspondence exists between the model and the ultrasonic attenuation observed in the same silica glass without irradiation. Some evidence for the role of hydrogen in low-frequency motions has been found[13] in acoustic attenuation.

SUMMARY

Measurements of the temperature dependence of spin relaxation of the atomic-hydrogen centers generated in Corning 7940 fused silica by gamma irradiation at 78°K indicate that a novel relaxation mechanism is present. The data are interpreted in terms of low-frequency vibrational modes having large, temperature-independent amplitudes. The preferred model which leads to this kind of motion considers the hydrogen center to be trapped in a "box" whose longest dimension is about 7 Å. The observed annealing behavior requires that there be some distribution in the structure of the hydrogen centers throughout the glass.

ACKNOWLEDGMENTS

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