PHYSICAL REVIEW B VOLUME 34, NUMBER 11 1 DECEMBER 1986

Fundamental radiation-induced defect centers in synthetic fused silicas: Atomic chlorine, delocalized E' centers, and a triplet state

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(Received 21 July 1986)

A series of synthetic fused silicas of diverse OH contents was subjected to 100-keV x irradiations at 77 K and investigated by electron-spin-resonance techniques at ~ 110 K or higher temperatures. Spectra were recorded at X-band frequencies (~ 9.2–9.3 GHz) both as the first derivative of absorption and in the high-power second-harmonic mode in order to bring out features not fully accessible by using one of these methods alone. In addition to the previously known E'_α, E'_γ, and oxygen-associated hole centers, three new defects were detected and characterized by computer line-shape simulation methods. These were atomic chlorine, a delocalized E' center (denoted E'_δ), and the first biradical to be reported in a-SiO_2. A sample-to-sample correlation of the radiation yields of these three new centers has been noted, leading to the suggestion that all three find their origins in specific chlorine-decorated precursor sites in the unirradiated glasses. Although significant chlorine impurities (> 100 ppm) may be ubiquitous in both type-III (high OH) and type-IV (low OH) fused silicas, the occurrence of chlorine-associated radiation-induced defects appears to be anticorrelated with the OH contents of the materials. Some possible technological implications of these findings are discussed.

I. INTRODUCTION

Amorphous silicon dioxide (a-SiO_2) is found in the cores of current generation low-loss optical fiber waveguides and as the gate oxide in silicon-based metal-oxide-semiconductor (MOS) transistors. In both technologies, the presence of impurities or structural defects may exert profound influences on device performance, particularly in radiation environments.[1–3] As a consequence, industrial processes have been evolved to maximize material purity and structural perfection. The one impurity which is most commonly present in synthetic fused silicas and thermally grown a-SiO_2 films is water (in the form of hydroxyl groups). Although benign in some applications, these OH groups have vibrational absorption bands which encroach on the wavelength windows of interest for optical communications.[2] Moreover, molecular hydrogen resulting from the radiolysis of hydroxyl groups has been implicated in the radiation-induced buildup of defect states at the Si/SiO_2 interface.[4] Thus, for many specific applications the impetus has existed to remove as much water as possible from the a-SiO_2 components. The ultimate sensitivities of these dry oxides to nuclear radiations should then be determined by the intrinsic defect structure of the a-SiO_2 phase—provided that no additional defects or impurities are introduced in the drying process.

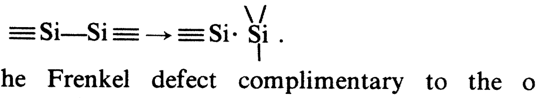
Radiation-induced defect centers in a-SiO_2 have been the objects of intensive study for over three decades.[5] Mostly as the result of electron spin resonance (ESR) investigations, three genera of defects have been elucidated in a-SiO_2 free of impurities other than water. They are the "E' center," $\equiv\text{Si}\cdot$,[6–9] the nonbridging oxygen hole center, $\equiv\text{Si—O}\cdot$[10,11] and the superoxide radical, $\equiv\text{Si—O—O}\cdot$ (Refs. 11 and 12) (where in each case the symbol $\equiv$Si represents a silicon atom bonded to three oxygens in the glass network and a dot denotes an unpaired spin). In principle, a nonbridging oxygen hole center and an E' center could be created as an intimate pair according to the reaction

$$\equiv\text{Si—O—Si}\equiv\;\rightarrow\;\equiv\text{Si—O}\cdot\quad\cdot\text{Si}\equiv\ . \tag{1}$$

However, in type-III silicas (prepared by flame hydrolysis of silicon tetrachloride and containing ~ 1200 ppm OH by weight) it has become evident that an important radiochemical mechanism for producing nonbridging oxygen hole centers is[13,14]

$$\equiv\text{Si—OH}\rightarrow\;\equiv\text{Si—O}\cdot+\text{H}^0\ . \tag{2}$$

Up until now, three E'-center variants had been tentatively identified in various forms of a-SiO_2.[15] All three have seemed to have in common an unpaired electron strongly localized in a dangling sp^3 orbital of a silicon pyramidally bonded to three oxygens in the glass network ($\equiv\text{Si}\cdot$). The prevailing view has been that most E' centers result not from the reaction of Eq. (1) but rather from the trapping of a hole at the site of an oxygen vacancy ($\equiv\text{Si—Si}\equiv$). Such a vacancy can either preexist in the glass as a member of a Frenkel defect pair, or it can be created by the impinging radiations.[16–18] An explanation as to why the unpaired spin should be fully localized on one silicon rather than two was provided in the asymmetric relaxation model of Feigl, Fowler, and Yip,[19,20] wherein the second silicon at the vacancy site relaxes into the plane of the three oxygens to which it remains bonded:



$$\equiv\text{Si—Si}\equiv\;\rightarrow\;\equiv\text{Si}\cdot\ \overset{\diagdown\,\diagup}{\underset{|}{\text{Si}}}\ . \tag{3}$$

The Frenkel defect complimentary to the oxygen vacancy is thought to be the peroxy linkage ($\equiv\text{Si—O—O—Si}\equiv$).[12,21] An excess of peroxy linkages relative to the number of oxygen vacancies can result from the "drying" of high-OH silicas by outgassing of hydrogen at elevated temperatures:[14,22–24]

$$\equiv\text{Si—OH HO—Si}\equiv\ \rightarrow\ \equiv\text{Si—O—O—Si}\equiv + H_2\uparrow\ . \tag{4}$$

Hydroxylation experiments involving H_2 gas permeation of low-OH silicas have indicated that reaction (4) is reversible.[22] This finding provided strong support for the widely held belief that OH groups tend to occur in pairs in a-SiO_2. The superoxide radical can be formed by hole trapping on a peroxy linkage or, alternatively, by the reaction of interstitial molecular oxygen with an E' center:[21]

$$\equiv\text{Si}\cdot + O_2 \rightarrow\ \equiv\text{Si—O—O}\ . \tag{5}$$

It is clear from the foregoing brief overview that the natures of the radiation-induced defect centers in high-purity a-SiO_2 are already known to depend strongly on a number of factors, including not only the final hydroxyl content of the material but possibly also the process by which it may have been "dried." Most "type-IV" fused silicas (< 10 ppm OH) are produced directly by plasma oxidation of $SiCl_4$. It has long been known that such low-OH synthetic silicas may contain high concentrations of chlorine.[25–27] In addition, the processing of SiO_2-on-Si structures sometimes includes an anneal step in a HCl ambient designed to remove water but which results in a concomitant buildup of chlorine near the interface.[28] Despite these not-uncommon examples of its presence in important a-SiO_2 technologies, little information seems to be available in the literature as to how chlorine is incorporated in the glass or how it might affect the formation of radiation-induced defects. The present ESR study, carried out on commercial type-III and IV fused silicas of various OH contents, succeeds for the first time in isolating radiation-induced defect centers associated with chlorine.

II. EXPERIMENTAL DETAILS

All of the samples investigated were in the form of 4-mm-diam rods cut into lengths $\simeq$2–3 cm. They included Suprasil 1 and W1 (1200 and 5 ppm OH, respectively) and a series of silicas of Japanese manufacture[29] prepared by various methods to achieve a range of OH contents (Table I). These were subjected to 100-keV x irradiation at 77 K (doses ranging from ~3–30 Mrad) and studied as functions of isochronal anneals to higher temperatures. ESR spectra were recorded on either a Varian E-9 or a Bruker ER 200 spectrometer operating at X-band frequencies (~9.2–9.4 GHz). First-derivative spectra were obtained using 100-kHz field modulation, while 50-kHz modulation was employed in the second-harmonic detection mode. The sample temperature was regulated by means of a stream of N_2 gas, permitting *in situ* anneals up to 473 K. Heat treatments to higher temperatures were accomplished by removing the samples to a laboratory furnace.

Several replicate samples of the 10-ppm-OH material were investigated, including one subjected to ^{60}Co γ rays at room temperature (dose 2.9×10^7 rads). A chemical analysis (spark source mass spectroscopy) performed on an aliquot of 10-ppm-OH material indicated the presence of ~3000 ppm chlorine.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Atomic chlorine

The samples containing $\geq$700 ppm OH displayed radiation-induced ESR spectra highly reminiscent of those already described in commercial type-III silicas such as Suprasil 1 or Spectrosil.[10,13,15] However, the three Mitsubishi Cables, Ltd. samples with lower water contents each exhibited a particular suite of resonance lines which have been unobserved (or uninterpreted by virtue of their low intensities) in the other silicas. Accordingly, special attention was devoted to the best exemplar of these new lines, which turned out to be the material containing 10 ppm OH (DN No. 2). Figure 1(a) reproduces a high-gain, first-derivative-mode spectrum obtained for a sample of this material at 105 K immediately following low-temperature x irradiation. The narrow central features driven off scale in this display are due to oxygen-associated hole centers (OHC's) and E' centers. Figure 1(b) is a computer simulation of the new features achieved under the assumption that they arise from interstitial

TABLE I. Sources, preparation methods, and nominal OH contents of the synthetic silica samples employed in this investigation. In all cases, the starting reagent was $SiCl_4$.

Manufacturer	Designation	OH content (ppm)	Preparation method
Heraeus	Suprasil W1[a]	~5	(Oxygen?) plasma
Mitsubishi	DN No. 1[b]	< 1	Ar plasma, Cl_2 added for lower OH
Mitsubishi	DN No. 2[b]	< 10	Ar plasma
Mitsubishi	DN No. 3[b]	~100	Ar plasma, H_2O added for higher OH
Mitsubishi	DN No. 4[b]	~700	Ar plasma, large H_2O addition
Mitsubishi	DN No. 5[b]	~800	Flame hydrolysis
Mitsubishi	DN No. 6[b]	~800	Flame hydrolysis
Heraeus	Suprasil 1[a]	~1200	Flame hydrolysis

[a] Product name.

[b] Arbitrary designator of specially provided sample.

atomic chlorine characterized by the distribution of g values and the "parallel" hyperfine structure (hfs) illustrated in Fig. 1(c). Other spin-Hamiltonian parameters employed in this simulation are listed in Table II.[30]

The simulated portions of the spectrum of Fig. 1(a) are here attributed to atomic chlorine on the following bases: (i) The observed "parallel" spectrum is seen to comprise a concentric pair of quarters with relative field splittings bearing the same ratio as the magnetic moments of the two abundant isotopes of chlorine. [^{35}Cl and ^{37}Cl are 75.4% and 24.6% abundant, respectively, each has spin $I=\frac{3}{2}$, and $\mu_N(35)/\mu_N(37)=1.20$.] (ii) The simulation was successfully accomplished using the aforementioned abundances and nuclear moments as constraints, and the values of $A_{\parallel}$ and $A_{\perp}$ which optimized the result were virtually identical to the published $3p$-state coupling constants for Cl^0.[31] (iii) Chlorine is the only chemical element with nonzero nuclear spin known to be present in the sample at sufficiently high levels to account for a multiline hyperfine spectrum of the observed intensity. (iv) The values of the hyperfine parameters derived in the simulation were in excellent agreement with those earlier determined[32] for Cl^0 in irradiated alkali-halide—alkali-borate glasses (Table II).

As was previously found to be the case for the spectrum of Cl^0 in the alkali-borate glasses,[32] the final success of the computer line-shape simulation was dependent on assuming a broad distribution of $g_{\perp}$ values derivable from the following approximate expressions originally developed for the isoelectronic O$^-$ ion in an axial environment:[33]

$$g_{\parallel} \simeq g_{\text{free electron}} \tag{6}$$

and

$$g_{\perp} \simeq g_{\parallel}(1+l\lambda/\Delta)\ . \tag{7}$$

In Eq. (7), λ is the spin-orbit coupling constant for Cl^0, l is a constant of order unity, and Δ is the axial-field splitting of the orbital degeneracy of the $p_x^2 p_y^2 p_z^1$ ground configuration. As before, the trial distributions in $g_{\perp}$ values were constrained by assuming Gaussian distributions in the energy splitting Δ (a presumed consequence of vitreous-state disorder).[32] It can be seen in Table II that the mean value of $g_{\perp}$ derived for Cl^0 in a-SiO$_2$ is substantially smaller than that found for the same atom in the alkali borate host. This empirical fact accounts for a considerable difference in the general appearances of the computed spectra [Fig. 1(b) of this paper vis-à-vis Fig. 1(b) of Ref. 32]. But in both cases the axial symmetry of the g matrices implies that the ions must be located in interstitial sites, since an orthorhombic g matrix would result if preferred bonds were to be formed with either one or two boron or silicon atoms.[34]

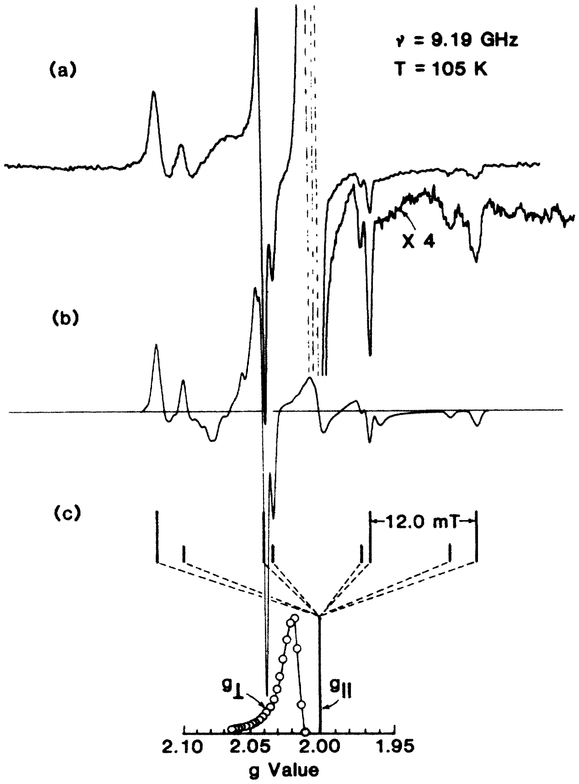


FIG. 1. (a) ESR first-derivative spectrum obtained at 105 K for a low-OH synthetic silica (DN No. 2) subjected to 100-keV x irradiation at 77 K. (b) Computer line-shape simulation of the atomic chlorine contribution to (a). (c) g-value distribution and ^{35}Cl and ^{37}Cl "parallel" hyperfine splittings adopted in carrying out the simulation of (b).

TABLE II. Spin-Hamiltonian parameters for radiation-induced atomic chlorine in amorphous hosts, as determined by computer simulation of experimental ESR line shapes. Hyperfine coupling constants pertain to ^{35}Cl.

	Value	
Parameter	Alkali borate glass[a]	Synthetic fused silica[b]
$g_{\parallel}$	1.997	2.0007
$g_{\perp}$[c]	2.063	2.027
$A_{\parallel}/g\beta$ (mT)	12.2	12.0
$A_{\perp}/g\beta$ (mT)	6.1	6.0

[a] Reference 32.

[b] This work, sample = DN No. 2.

[c] Ensemble average of skew-symmetric distribution as in Fig. 1(c).

B. A new E' center

The unbroken curve in Fig. 2(a) represents the "central" region of the spectrum of Fig. 1(a) as recorded on an expanded field scan and at a greatly reduced spectrometer gain. The dashed curve is a computer simulation comprised of a weighted sum of the three component spectra shown in Fig. 2(b). Component spectra labeled E'_{α} and E'_{γ} correspond to previously delineated E'-type centers and were synthesized using g-value distributions essentially identical to those given elsewhere[15] (average g matrices for these centers are listed in Table III). The narrow component labeled E'_{δ} is a "new" signal in the sense that it has never been observed (except possibly as a

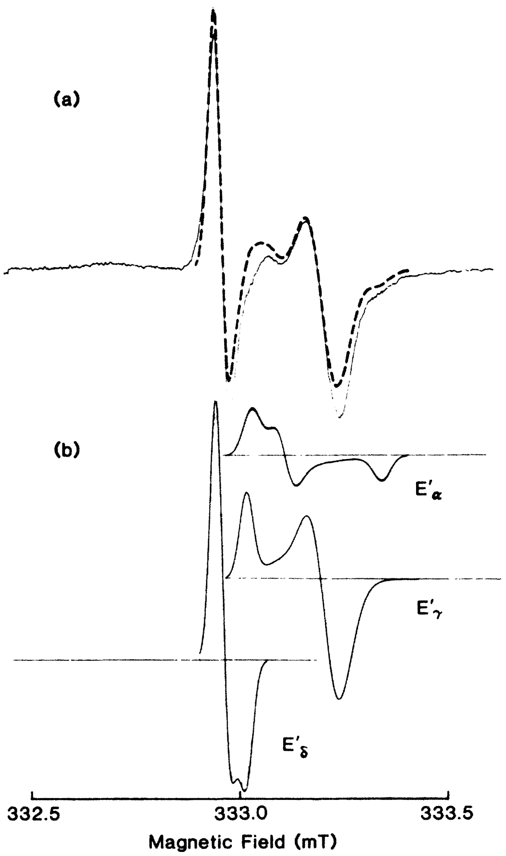


FIG. 2. ESR first-derivative spectra corresponding to the "central" region of Fig. 1. (a) Experimental spectrum (solid curve) and computer simulation (dashed). (b) Individual components which comprise the computed spectrum of (a).

weak unresolved shoulder) in the most commonly studied high-purity synthetic silicas such as Suprasil 1, 2, or W1, or Spectrosil. Although the authors are unaware of any published accounts of such a line in any other forms of bulk fused silica, a similar resonance was reported very recently in a thermally grown oxide on silicon.[35,36]

The fact that the new sharp-line spectrum appears to share one principal g value with the traditional E' centers (Table III) is immediately suggestive of the possibility that the defect responsible might be another species of E' center. To further test this notion, a continuous-wave (cw) microwave saturation experiment was carried out on the complex central-line spectrum with the results shown in Fig. 3. Here, it can be seen that the room-temperature saturation properties of the component denoted E'_δ are essentially identical to those of the co-present E'_γ center. Moreover, both curves effectively reproduce the behavior previously presented for E' centers in irradiated Suprasil 1.[8] This finding alone provides a strong basis for identifying E'_δ as a fourth species of E' center in a-SiO$_2$. As was the case for the other variants,[7,8,15] conclusive characterization of this new center ultimately hinges on the observation and analysis of ^{29}Si hyperfine structure (see Sec. III C).

TABLE III. Principal-axis g values for several E'-center variants in a-SiO$_2$.

	$E'_\alpha{}^{a}$	$E'_\gamma{}^{a}$	$E'_\delta{}^{b}$
g_1	2.0018	2.0018	2.0018
g_2	2.0013	2.0006	2.0021
g_3	1.9998	2.0003	2.0021

[a] Ensemble average of statistical distribution, after Ref. 15.
[b] This work. Used in computer simulation of Fig. 2.

C. Broad-line spectra: ^{29}Si hfs of E'_δ and evidence for a triplet state

The search for ^{29}Si hfs of the E'_δ center was conducted in the high-power second-harmonic mode, as was previously proven to offer the best signal-to-noise ratio.[15] The upper curve in Fig. 4(a) illustrates the broad-line spectrum observed at 105 K for the 10-ppm-OH sample (DN No. 2) immediately following x irradiation. For comparison, the lower curve in Fig. 4(a) is a computer simulation of the absorption curve of atomic chlorine, the first derivative of which is shown in Fig. 1(b). It is evident that the asymmetric signature of Cl^0 is prominent in the broad-line spectrum so long as the sample is held at temperatures ≤ 105 K. However, a 10-min anneal at 50 °C proves sufficient to bleach the Cl^0 spectrum totally, leaving a progression of more-or-less symmetrically disposed shoulders and peaks shown in Fig. 4(b). The outer pair of lines visible in all three parts of the figure [but best resolved in Fig. 4(c)] is identical with the 42-mT ^{29}Si hfs which ubiquitously characterizes the α, β, and γ variants of the E' center in a-SiO$_2$.[15] To the authors' knowledge, the remainder of the shoulder structure in Fig. 4(b) has not been reported previously. The present section is concerned with determining the origins of these new broad-line features.

Isochronal annealing experiments performed on a γ-irradiated sample indicated that the bleaching rate of the ramplike shoulders measured at ±10 mT (with respect to the "central" E' lines) is identical with the bleaching rate

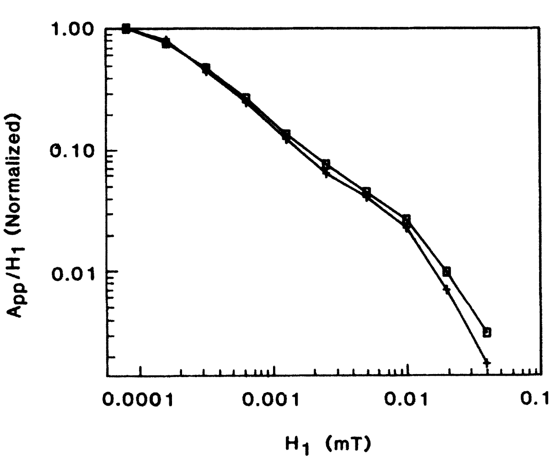


FIG. 3. Room-temperature continuous-wave microwave saturation characteristics of E'_γ centers (squares) and E'_δ centers (crosses) in an x-irradiated low-OH synthetic silica.

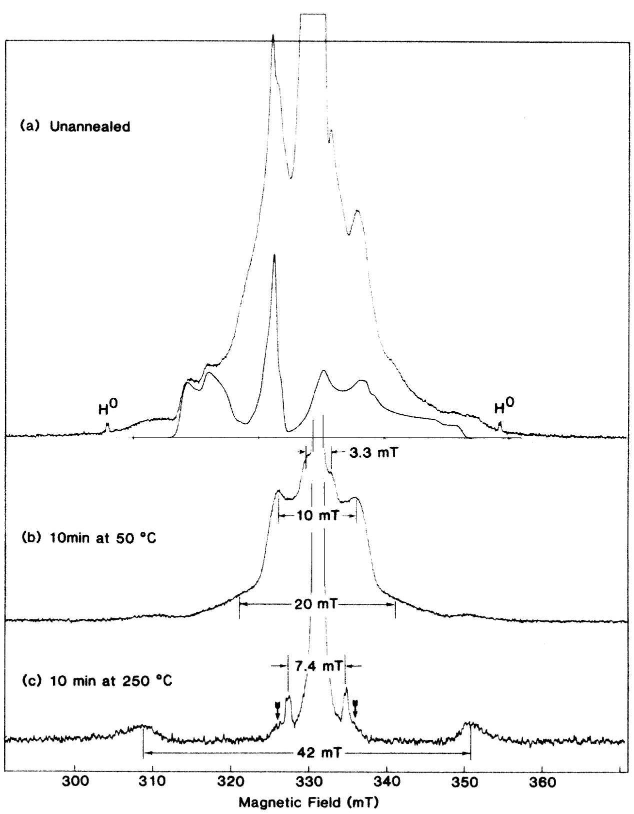


FIG. 4. High-power second-harmonic mode spectra recorded at 110 K for a low-OH synthetic silica (DN No. 2) (a) immediately following 100-keV x irradiation at 77 K and (b) and (c) following subsequent heat treatments to higher temperatures. Experimental parameters were identical for all three traces except for a tenfold increase in gain for curve (c). The low curve in (a) is a computer simulation of the ESR absorption curve of atomic chlorine.

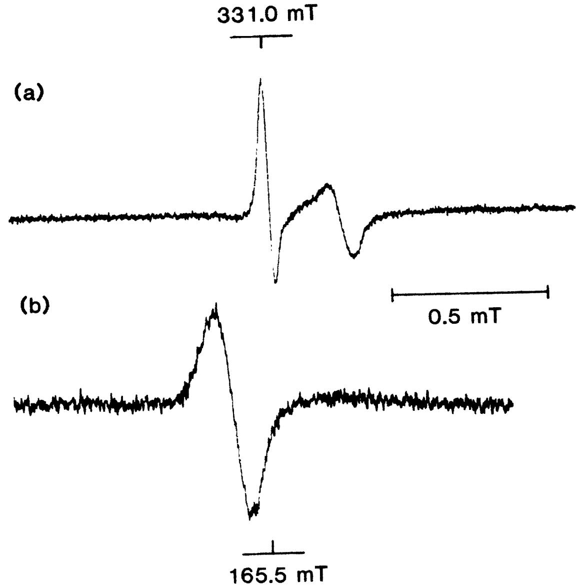


FIG. 5. ESR first-derivitive spectra obtained at room temperature for an x-irradiated low-OH synthetic silica (DN No. 2). (a) Spectral region about $g = 2$. (b) Spectral region about $g = 4$. Both spectra were recorded on the same chart by changing only the center fields (indicated), relative gain factors (as described in the text), and the vertical offset.

for the steeper pair of shoulders arbitrarily measured at ±6 mT. (The inner pair of shoulders split by ~3 mT was found to bleach more slowly.) Moreover, none of these broad lines bleached in exactly the same way as any of the sharp E' "central lines" of Fig. 2. These results (not illustrated) suggested that much, if not all, of the inner shoulder structure may arise from sources other than hfs of E' centers and, in particular, that the features split by ~12 and 20 mT may arise from a single paramagnet entity.

Among the explanations considered for the 10- and 20-mT shoulder structure [see, Fig. 4(b)] was a defect characterized by an $S = 1$ ground state.[37] To test for this possibility, a search was carried out for resonance absorptions in the region $g_{\text{eff}} = 4$. Just such a resonance was located at approximately half of the resonance field of the E' centers recorded at the same microwave frequency: The spectrum of Fig. 5(b) was obtained at an overall spectrometer gain [(modulation)×(amplifier gain)×$(\text{power})^{1/2}$] 8840 times greater than that required to record the E'-center spectrum of Fig. 5(a). Most of this added gain was accomplished by means of a 57-dB increase in the microwave power. Measurements at intermediate power settings indicated the intensity of the half-field line to be a slightly sublinear function of the square root of the microwave power from 0.05 to 50 mW. All of these observations are compatible with the conclusion that the half-field line is a weakly allowed $M_S = -1 \leftrightarrow M_S = +1$ transition of a triplet state characterized by $g \simeq 2.00$.[38] Additional experiments were necessary to ascertain whether, in fact, any of the shoulder structure described above actually comprises the $-1 \leftrightarrow 0$ and $0 \leftrightarrow +1$ transitions of this triplet.

Figure 6(a) illustrates a high-power, fast-passage, first-derivative-mode spectrum (unbroken curve) of a sample of DN No. 2 which had been subjected to a large cumulative x-ray dose ($\sim 1.5 \times 10^7$ rads).[39] Figure 6(b) shows the high-power second-harmonic mode spectrum of this same sample. Clearly apparent in Fig. 6(a) is a symmetric "doublet" characterized by a peak-to-peak splitting of ~13 mT, which corresponds somewhat imperfectly with the 10-mT doublet noted in the second-harmonic mode, Fig. 6(b). The dashed curves in Figs. 6(a) and 6(b) are computer line-shape simulations of the first-derivative and absorption curves, respectively, of the $-1 \leftrightarrow 0$ and $0 \leftrightarrow +1$ transitions of a triplet state characterized by the spin-Hamiltonian parameters of Table IV. Good agreement between the experimental and computed spectra can be noted in Fig. 6(a) while less satisfactory agreement is found in Fig. 6(b). In this context, it should be commented upon that paramagnetic centers which are subject to severe microwave saturation effects (e.g., E' centers) may be difficult to observe in the high-power first-derivative

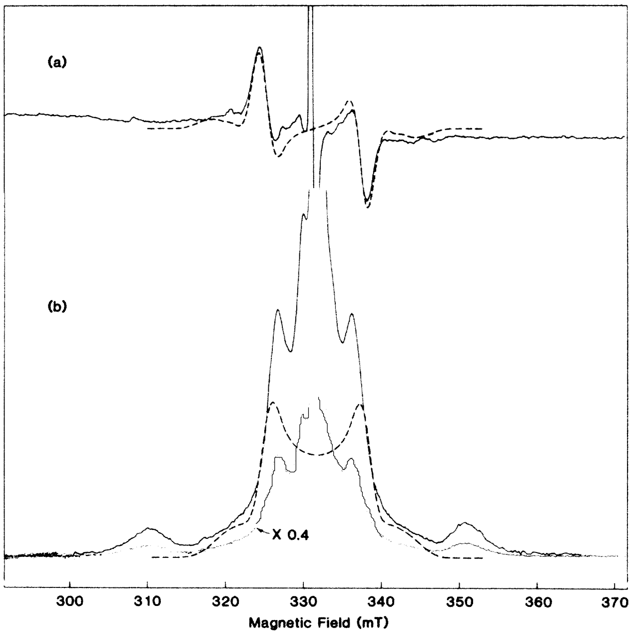


FIG. 6. (a) ESR first-derivative spectrum and (b) high-power second-harmonic mode spectrum recorded at 225 K for a low-OH synthetic silica (DN No. 2) x irradiated at 77 K. Microwave power levels were 1.5 and 50 mW for (a) and (b), respectively. Dashed curves are computer simulations of (b) the absorption curve of an $S=1$ state and (a) the first derivative of this absorption, using the spin Hamiltonian parameters of Table IV.

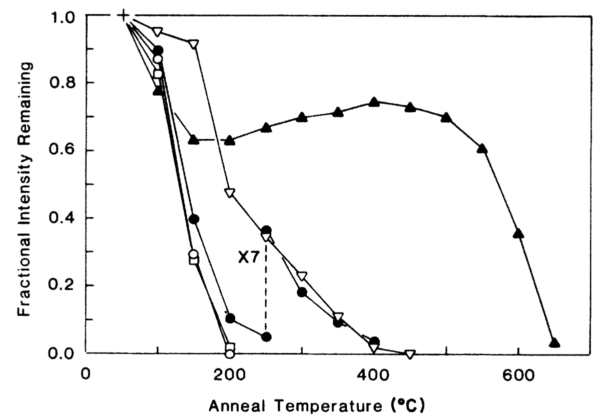


FIG. 7. Isochronal anneal curves (10 min at each temperature) for various ESR spectral manifestations of x-ray-induced defects in a low-OH synthetic fused silica (DN No. 2). Open symbols represent amplitudes of first-derivative spectra, while solid symbols portray amplitudes of high-power second-harmonic mode spectra. ○, triplet state, as in Fig. 6(a). □, half-field line, as in Fig. 5(b). ▽, E'_δ center, as in Fig. 2. ▲, 42-mT hfs of E'_γ centers, as in Fig. 4(c). ●, Amplitude measured at the position of the low-field arrow in Fig. 4(c). All data were acquired at 323 K.

mode but more easily acquired in the high-power second-harmonic mode [note the presence of the 42-mT doublet in Fig. 6(b) and its absence in Fig. 6(a)]. Thus, it was hypothesized that the 13-mT doublet of Fig. 6(a) may be essentially a single resonance, while the 10-mT doublet of Fig. 6(b) might comprise several overlapping spectra.

An isochronal annealing experiment was carried out on the sample described in the preceding paragraph. This study tracked the amplitudes of all major central-line and broad-line spectra under both normal fast-passage and high-power second-harmonic mode conditions. It is clear from the plotted data of Fig. 7 (specifically, the open circles compared with the open squares) that the 13-mT doublet of Fig. 6(a) bears an excellent correlation with the half-field line of Fig. 5(b). (The integrated intensity of the half-field line was determined to be $\sim 4\times 10^{-4}$ times the intensity of the doublet.) This association of the 13-mT structure with the half-field line completes the isolation of the triplet state.

TABLE IV. Spin-Hamiltonian parameters for $S=1$ biradical in x-irradiated low-OH synthetic fused silica. Measurement temperature = 225 K.

Parameter	Value[a]
$\lvert D\rvert/g\beta$ (mT)	13.4
$\Delta\lvert D\rvert/g\beta$ (mT)[b]	2.0
$\lvert E\rvert/g\beta$ (mT)	0
g	2.002[c]

[a] Used for computer simulation of Fig. 6.
[b] Halfwidth of Gaussian distribution in $\lvert D\rvert$.
[c] A value of 2.003 is calculated from the position of the half-field line in Fig. 5 (see, Ref. 38).

On the other hand, the amplitude of the 10-mT doublet observed in the second-harmonic mode (solid circles in Fig. 7) is less than perfectly correlated with the aforementioned manifestations of the triplet. In fact, above 200 °C (where the triplet state is totally absent) the amplitudes of the 10-mT features are seen to correlate rather well with the amplitude of the E'_δ central line (open triangles). On this basis it is suggested that the 10-mT doublet structure which survives the 250-°C anneal [marked by arrows in Fig. 4(c)] (Ref. 40) is the ^{29}Si hfs of the E'_δ center. By extension, it is proposed that much of the intense 10-mT doublet observed in the second-harmonic mode before warming above 225 K [Fig. 6(b)] also arises from this source. That is, all of the broad-line structure in Fig. 6(b) not accounted for by the dashed triplet-state simulation is postulated to be ^{29}Si hfs of E' centers.

D. Spin population determinations

Paramagnetic spin concentrations were determined by double numerical integration of the fast-passage first-derivative spectra and comparison to the results for a calibrated pitch standard.[41] Data for the E' centers and H^0 were obtained at the lowest possible microwave power setting (~ 0.2 μW) to minimize errors due to microwave saturation. The less saturable Cl^0 and oxygen-hole-center (Ref. 42) spectra were recorded at a power level of 10 mW. Table V (Ref. 43) lists the results for a series of samples measured at ~105 K following a 1.5 h exposure to 100-keV x rays at 77 K (dose $\sim 4.5\times 10^6$ rads). It can be seen that the yields of atomic hydrogen generally correlate with the hydroxyl contents of the samples as provided by the manufacturers. It is also apparent that increasing quantities of radiolytic atomic chlorine are encountered as the silicas grow drier. Additionally, in the suite of samples provided by Mitsubishi there seems to be a positive correlation between the occurrence of Cl^0 and the observations of both the E'_δ center and the triplet state (as well as a possible anticorrelation between Cl^0 and the OHC's). However, Suprasil W1 is seen to behave somewhat differently, indicating the probable influences of processing variables which remain proprietary to the respective manufacturers.

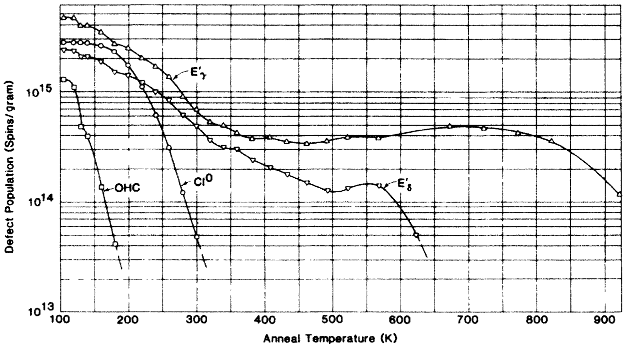


FIG. 8. Isochronal anneal curves (5 min at each temperature) for selected defect populations in a low-OH synthetic silica (DN No. 2) following a ~3-Mrad x irradiation at 77 K. Data were acquired at 105 K.

Figure 8 illustrates in absolute quantitative terms the isochronal anneal characteristics of the four numerically dominant defect centers in DN No. 2 following a 3-Mrad x irradiation at 77 K.[43] Inspection of these data elicits some speculations on the mechanisms by which the various defects thermally anneal and, by projection, their mechanisms of formation. First, note can be taken of the fact that the sharp drop in OHC population between 120 and 130 K corresponds to decreases of the same absolute magnitude in the E'-center populations. One way this observation could be interpreted would be to assume that most of the OHC's decay by the reverse reaction of Eq. (1) and, by implication, that these OHC's may have been created by reaction (1).[44] Of course, the vast majority of the (more numerous) E' centers must have been created by another path. The correlation of the E' population with the Cl^0 yield (Table V) suggests the possible importance of the analogous reaction

$$\equiv\text{Si—Cl}\rightarrow\equiv\text{Si}\cdot+\text{Cl}^0\,. \qquad (8)$$

If Eqs. (1) and (8) were to hold, the overall E' population should equal the sum of the OHC and Cl^0 concentrations. A number of possible explanations can be offered for the fact that the combined OHC and Cl^0 populations as measured fall short of this prediction by a factor of about 2. These include failure to fully correct for microwave saturation effects and the intrinsic difficulty in numerically integrating very broad spectra such as those of the OHC and Cl^0. Considering only the *shapes* of the anneal curves of Fig. 8 and allowing their absolute scale factors to be adjustable parameters, a good congruency could be achieved between the sum of the OHC and Cl^0 populations and the sum of the E'-center populations between 100 and ~300 K. Of course, at higher temperatures no such correspondence obtains. It is suggested here that the lingering presence of some E' centers to anneal temperatures as high as 900 K in the apparent absence of any measurable anionic hole traps can be explained by postulating the dimerization of some of the atomic chlorine initially produced, resulting in the formation of interstitial chlorine molecules. Since the diffusivity of Cl_2 in the a-SiO_2 network is expected to be many orders of magnitude lower than that of Cl^0, the reverse reaction of Eq. (8) would be thwarted to the extent that such dimerization had occurred.

E. Models for the new defect centers

It was suggested in Sec. III C that the 10-mT shoulder structure in Fig. 4(c) [and part of the 10-mT doublet in Fig. 4(b)] is ^{29}Si hfs of the E'_δ center. The viability of this postulate will now be examined. First, note can be taken of the fact that the 10-mT doublet of Fig. 4(c) is fully as

TABLE V. Defect yields in several synthetic silicas of diverse OH contents, determined at 105 K immediately following 100-keV x irradiation at 77 K (dose $\sim 4.5\times 10^6$ rads).

		Defect populations (10^{12} spins/g)					
Sample	OH content (ppm)	H^0	Cl^0	OHC	E'_γ	E'_δ	Triplet
Suprasil W1[a]	~5	330	740	13 000	1900	0	0
DN No. 1	<1	3	2400	1400	4300	1500	170
DN No. 2	<10	8	5000	1600	8300	4200	620
DN No. 3	~100	430	1300	7000	3800	260	150
DN No. 4	~700	4600	590	4450	4100	0	70
DN No. 5	~800	6900	110	5300	3400	0	30
DN No. 5	~800	11 000	110	4900	2400	0	18
Suprasil 1	~1200	10 500	0	3100	1700	0	12

[a] The sample used here had been x irradiated four years earlier, at which time the H^0 and OHC yields were found to be approximately 3 times lower than presently measured.

intense as the 42-mT doublet of the E'_γ centers—even though the number of E'_δ centers surviving the 250-°C anneal is only $\sim\frac{1}{3}$ of the surviving E'_γ centers (see Fig. 8). Second, attention is called to the fact that the relative magnitudes of the ^{29}Si hfs splittings imputed to the respective E' species imply that the spin density per silicon atom for E'_δ must be approximately four times less than that for E'_γ. (It is to be recalled that for E'_γ, $\sim 85\%$ of the spin density is confined to an sp^3 hybrid orbital of a single silicon atom.[7]) On these bases, it is proposed that E'_δ comprises an unpaired spin delocalized over *several* silicon atoms, which for simplicity will be assumed to be chemically equivalent.

Specifically, the model which is suggested here envisions synthetic silicas of low water content to incorporate chloride ions in groups of four, decorating SiO_4 vacancies in an otherwise continuous random network [see schematic illustration in Fig. 9(a)]. Such structures would be analogous with the presumed pairwise occurrence of OH groups in a-SiO_2 and in more complete analogy with the existence of OH-decorated SiO_4 vacancies in α quartz.[45] If a defect were to be created at such a site according to Eq. (8), a chlorine atom would be ejected into a distant interstitial position, leaving behind a cavity containing three chloride ions and one unpaired electron. This cavity would be bounded by four silicon atoms, each with an sp^3 orbital projecting into the cavity and three backbonds to oxygens in the glass network. As schematically laid out in Fig. 9(b), the E'_δ center is postulated to be just such a defect, wherein the unpaired spin is delocalized rather equally over the four silicons. (Since no evidence is found for hfs attributable to ^{35}Cl and ^{37}Cl nuclei, it is necessary to further posit that the unpaired spin experiences negligible mixing with the atomic orbitals of the chlorines.) Under this model the ^{29}Si hyperfine splitting of E'_δ would be predicted to be ~ 4 times smaller than that of E'_γ, as observed.

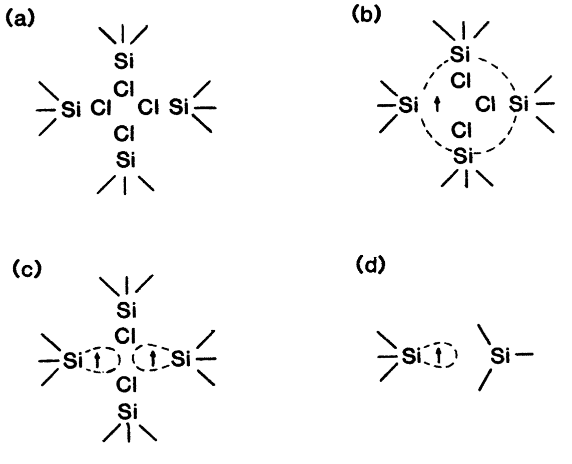


FIG. 9. Proposed models for defect centers in a-SiO_2 containing chlorine. (a) Chlorine-ion decorated SiO_4 vacancy in unirradiated glass. (b) E'_δ center. (c) Triplet state. (d) E'_γ center. Configurations (a) through (c) are electrostatically neutral. The right-hand silicon in (d) represents a net charge of +1.

The probability of finding a ^{29}Si nucleus at the site of an ordinary E'_γ center is 0.047, the natural abundance of that isotope. By contrast, the probability of finding a single ^{29}Si at the delocalized site postulated for the E'_δ center is $4(0.047)(0.953)^3 = 0.163$. This statistical factor therefore may explain the disproportionate intensity of the 10-mT doublet in Fig. 4(c) *vis-à-vis* the intensity of the 42-mT hfs of the more populous E'_γ center, as discussed above.

The proposed model is also capable of explaining one other facet of the E'_δ phenomenology, namely, the effective isotropy of its g matrix (see Table III). It is to be recalled that the near axial symmetry of the g matrix of the E'_γ center is associated with the silicon $3p$ contribution to the single sp^3 hybrid orbital which comprises the ground-state wave function.[46] This anisotropy would be averaged to zero were the unpaired spin to be delocalized over all four tetrahedral hybrid orbitals of a single silicon. It is just such a model that is here proposed for E'_δ, with the only difference being that the four tetrahedral orbitals project *into a cavity* instead of outward from a central atom.

As is apparent from Table V, there is a correlation between the occurrence of E'_δ and the newly characterized triplet state. It is thus reasonable to suggest that these two defects may find their origins in similar precursor structures. Furthermore, it is necessary to model the triplet state in such a way that the two unpaired spins which comprise the paramagnetic entity are constrained to a spatial separation large enough to yield the rather small axial-field splitting of 13.4 mT determined experimentally. These then are the bases for the model for the triplet state schematically diagrammed in Fig. 9(c), wherein the two unpaired spins are localized in dangling sp^3 orbitals of silicons in different locations in a cavity now occupied by only two chloride ions. A simple point dipole-dipole calculation[47] using the measured value of $|D|$ gives an estimate of 5.2 Å for the interelectron distance. This result compares favorably with the silicon-silicon distances of 4.9 to 5.9 Å measured across an (unrelaxed) SiO_4 vacancy in the α-quartz lattice.

In the foregoing discussion, the "doublet" structure with an approximate 3.3-mT splitting [Fig. 4(b)] is left unaccounted for. It is deemed unlikely that this structure is a manifestation of another triplet state, since the half-field absorption was found to disappear rather abruptly at 200 °C (Fig. 7) while shoulders with $\sim$3-mT splittings persisted to higher temperatures. One possibility is that these lines are the outer members of a hyperfine triplet due to a nitrogen-associated center first reported[48] as a laser-induced defect in Suprasil 1 and subsequently found in the same material following low-temperature x irradiation and thermal treatment.[49]

IV. CONCLUDING REMARKS

A series of commercial synthetic silicas of diverse OH contents has been investigated by ESR methods after low-temperature x irradiation. In the course of this work, three new defect species were detected and characterized for the first time in a-SiO$_2$: (i) interstitial atomic chlorine, (ii) and E'-type defect delocalized over four silicons, and (iii) a triplet state. The occurrences of all three new defects were generally found to be positively correlated, leading to proposed models for defects (ii) and (iii) which involve chloride ion clusters as precursors. Since the specific yields of all three defects were negatively correlated with the OH contents of the experimental samples and one of the drier samples was independently determined to contain an extremely large chloride content ($\sim$3000 ppm), it is tempting to interpret these results as indicating that the drying processes employed in producing these silicas result in the substitution of chorides for hydroxyl groups. But in view of reports of choride contents as high as 600 ppm in *high-OH* silicas,[27] the declining yields of atomic chlorine with increasing hydroxyl contents (Table V) might alternatively be ascribed to the rapid scavenging of radiolytic Cl^0 by reaction with the increasing yields of radiolytic H^0. Certainly, the observed instability of the triplet state at room temperature *in the high-OH samples only*[39] is reasonably attributed to its reaction with diffusing radiolytic molecular hydrogen.[13,14]

Although $S=1$ states have previously been described in crystalline α quartz,[47,50–52] the present study is believed to constitute the first report of a triplet defect in *amorphous* SiO$_2$ (and possibly in any inorganic glass). It should be remarked that the largest principal-axis g shift determined for the present $S=1$ defect ($\leq +0.001$) is substantially smaller than those found for certain of the triplet states in quartz [$+0.17$ (Ref. 47) and $+0.02$ (Ref. 50)]. Thus, while the latter have been deduced to arise from holes trapped on spatially separated oxygen ions (see, particularly, Ref. 47) the present data are more consistently interpreted as manifestations of a biradical comprised of dangling orbitals on separate silicons. As such, the present defect should be more closely related to the so-called E'' centers[51,52] in quartz.

More work will be necessary to assess the full implications of the present study with respect to the radiation sensitivity of fiber optics or MOS devices which, by virtue of their processing histories, may contain chloride impurities. There is some evidence that certain low-OH pure-silica-core optical fibers marketed by Mitsubishi are relatively rad hard *at room temperature*.[53] However, the results epitomized in Fig. 8 suggest that the thermal fading of damage incurred at lower temperatures could be slow due to the metastability of radiolytic atomic chlorine in the low-temperature regime. Preliminary data obtained on irradiated optical fibers drawn from similar preform materials have tended to validate this prediction.[1,54] As concerns MOS technology, it might be noted that all of the defects delineated in the present study are electrostatically neutral and would therefore not *per se* degrade the operation of such devices, unless the silicon represented in Eq. (8) were at the interface, or if charge carriers were injected into the oxide layer. In the latter event, the defect structures of Figs. 9(b) and 9(c) could trap injected holes while the interstitial chlorine atoms could trap electrons. Moreover, to the extent that any of the radiolytic Cl^0 should dimerize, the counterpart E'-type defects would become permanent positive charge trapping sites with no possibility of thermal annealing below 600 °C (Fig. 8).

ACKNOWLEDGMENTS

The authors are indebted to H. Tanaka (Mitsubishi Cables, Ltd.) for providing the crucial samples together with details of their preparation. K. J. Long (Sachs-Freeman Associates) is thanked for assistance with the initial stages of the experiment.

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[30] Due to the smearing effect of the distribution in $g_\perp$ values, it was not possible to obtain a direct measure of $A_\perp$. However, the success of the simulation of Fig. 1(b) tends to validate the imposed constraint that $|A_\perp| \simeq |A_\parallel|/2$. A small distribution in $A_\parallel$ values (half width ~ 0.3 mT), uncorrelated with the g-value distribution, was introduced to optimize the simulation.

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[36] In Ref. 35 the "new" E' line was computer simulated under a different model hypothesis for the g matrix than was employed in the simulation of the E'_δ component of Fig. 2. At present it is not possible to say if this discrepancy arises from a lack of uniqueness in one or both simulations or if, on the other hand, it implies that the two new centers are unrelated.

[37] Another explanation considered for the broad-line structures with splittings of ~ 10 and 20 mT was a defect undergoing hyperfine interactions with more than one chlorine. However, Cl_2^- was ruled out on the grounds that the spectrum exhibited neither the expected (asymmetric) line shape nor the correct hfs splittings [see, D. L. Griscom, P. C. Taylor, and P. J. Bray, J. Chem. Phys. **50**, 977 (1969)]. Moreover, computer simulations of these broad-line features assuming a hyperfine interaction with *three* chlorine atoms were attempted but could not be achieved under the constraints of the model (statistically imposed weighting factors on the individual hfs components).

[38] The half-field line of Fig. 5(b) was obtained by setting the center field on the microprocessor-controlled field controller to half of the center field employed in obtaining the trace of Fig. 5(a). According to the manufacturer's literature, both settings should have been accurate to ≤ 0.1 mT.

[39] The irradiation history of this particular sample (containing 10 ppm OH) included a 1×10^7-rad irradiation followed by a two-month period at room temperature (RT) and a subsequent 5×10^6-rad dose at 77 K. Spectra obtained at intermediate times indicated that the spectral features identified with the triplet state bleached very little at RT. By contrast, in the samples of higher OH contents, the triplet manifestations faded at RT in periods of the order of minutes.

[40] Also apparent in Fig. 4(c) is a 7.4-mT doublet which arises from a numerically minor defect type involving a proton [see, J. Vitko, Jr., J. Appl. Phys. **49**, 5530 (1978)]. By means of annealing experiments, the 7.4-mT doublet was easily separable from the 10-mT doublet here attributed to ^{29}Si hfs of E'_δ.

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[42] For present purposes, no effort was made to separate the spectral contributions of the nonbridging-oxygen hole centers from those of the superoxide radical, although it was clear from the line shapes that the latter tends to predominate over the former in the drier forms of silica (see, Ref. 10).

[43] For simplicity, the quantities labeled "E'_γ centers" in Table V and Fig. 8 actually represent the *combined* concentrations of E'_γ and E'_α. Since the latter is effectively bleached out above ~ 150 K (Ref. 15), the distinction is moot at higher temperatures.

[44] Alternatively, the sharp decay steps in both the OHC and the E' center populations near 130 K could be due to their separately reacting with diffusing hydrogen atoms (see, e.g., Ref. 14).

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