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E' center in glassy SiO_2: ^{17}O, ^{1}H, and "very weak" ^{29}Si superhyperfine structure

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Electron-spin-resonance spectra have been obtained at 9.1 and 35 GHz for E' centers induced by γ irradiation in a number of high-purity commercial fused silicas and in a suite of glassy SiO_2 samples of varying degrees of enrichment (or depletion) in the magnetic isotopes ^{17}O and ^{29}Si. Computer simulation of the spectra of the ^{17}O-enriched samples indicates the existence of a weak superhyperfine (shf) interaction ($a_{\text{meas}}/a_{\text{atomic}} \approx 5 \times 10^{-4}$) with oxygens in three chemically equivalent near-neighbor sites. "Weak" shf structure characterized by $a \approx 8$ G observed in samples containing $\leqslant 50$ at.% ^{29}Si is shown to be due to protons present as impurities. An unresolved broadening of the spectra of samples containing $\geqslant 50$ at.% ^{29}Si is ascribed to "very weak" shf interactions with next-nearest-neighbor silicons. These findings, together with a comparison of the g matrices of bulk and surface E' centers, support the notion that the structure of the E' center in glassy silica is essentially identical to that in α quartz; i.e., both comprise asymmetrically relaxed oxygen vacancy defects.

I. INTRODUCTION

The E' center has long been recognized as a fundamental radiation-induced paramagnetic defect type in high-purity silicon dioxide. Since its early observation and characterization by Weeks and Nelson,[1] several E' variants have been identified, and these are conventionally differentiated by appending the subscripts 1, 2, 4, or s. Electron-spin-resonance (ESR) studies of irradiated α quartz have established that the E_1' center comprises an unpaired electron spin highly localized in an sp^3 hybrid orbital of a single silicon located near a normal crystallographic site. The principal evidence for this conclusion was the observation by Silsbee[2] of a "strong" hyperfine (hf) doublet of the appropriate magnitude ($A_{\text{iso}} \sim 410$ G) and intensity consistent with the 4.7 at.%-abundant ^{29}Si isotope ($I = \frac{1}{2}$), with principal-axis orientations parallel to normal Si—O bond directions. The development of more detailed structural models for the E_1' center was hampered from the beginning by the observation of so-called "weak" hyperfine structure (hfs) ($A_{\text{iso}} \sim 8$ G) presumed to be due to two more ^{29}Si nuclei at somewhat more distant positions.[2] An ingenious model explanation was eventually tendered by Feigl, Fowler, and Yip,[3] who suggested that the spin could be localized at the site of an asymmetrically relaxed oxygen vacancy. Specifically, it was postulated that the silicon which retained the spin also retained its tetrahedral hybridization, while the counterpart silicon on the opposite side of the vacancy relaxed into the plane of the three oxygens to which it remained bonded [Fig. 1(a)]. Theoretical

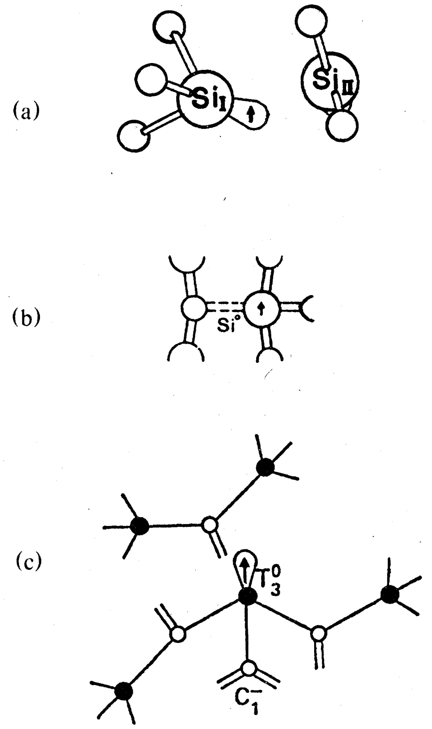

FIG. 1. Highly specific models for the E' center in bulk SiO_2: (a) Asymmetrically relaxed oxygen vacancy model due to Feigl, Fowler, and Yip (Ref. 3); (b) and (c) models specific to glassy silica proposed in Refs. 18 and 20, respectively. In (a) and (b), large circles represent silicons and small circles oxygens. In (c), silicons are portrayed by filled circles, and C_1^- is a nonbridging oxygen. Arrows indicate unpaired electronic spins.

calculations by Yip and Fowler[4] and by Gobsch *et al.*[5] showed that one of the two "weak" hfs doublets could be due to the second, relaxed silicon. Calculations of the g tensor by Gobsch *et al.*[5] also supported the Feigl-Fowler-Yip model. Nevertheless, the second "weak" doublet proved to be a stumbling block in both calculations.

As shown by Weeks,[6] the E_2' center in α quartz is distinguished by a weak hf interaction with a proton ($A_{\parallel} \approx 1.35$ G, $A_{\perp} \approx 0.2$ G) with principal axes roughly coparallel with those of the g tensor. Once again, a "strong" ^{29}Si hf doublet was observed ($A \approx 412$ G for the magnetic field $\vec{H}$ parallel to the c axis), and this datum was adduced to show that the E_2' center, like the E_1' defect, comprises an unpaired spin strongly localized in a hybrid orbital of a single silicon.[6] Feigl and Anderson[7] called attention to the fact that there exist in α quartz two classes of Si—O bonds[8] and that the unique axes of the E_1' and E_2' centers are roughly parallel to the "short" and "long" bonds, respectively. Thus, the Feigl-Fowler-Yip model[3] recognized that two inequivalent relaxations are possible at the site of an oxygen vacancy and postulated that the one relaxation results in the formation of an E_1' center, while the other (energetically less favorable) relaxation can be stabilized by a nearby proton to yield the E_2' species.

More recently, Halliburton *et al.*[9] have characterized the E_4' center[1] in some detail, showing the four-line hfs observed at X-band frequencies to be due to a hyperfine interaction with a single hydrogen nucleus under conditions that the hf and nuclear Zeeman energies have approximately the same magnitudes. It appears that the E_4' center may result from the trapping of a radiation produced hydrogen atom at the site of a neutral oxygen vacancy, resulting in an E'-type defect with a captive H^- ion.[10]

The surface E' center, E_s', has been detected by Hochstrasser and Antonini[11] on pristine surfaces of various α quartz and fused silica samples crushed under ultrahigh vacuum. E_s' is characterized[11] by g shifts and "strong" ^{29}Si hf splittings slightly larger than those which typify the bulk E' centers. The model for the surface E' center is necessarily simpler than any of those of Fig. 1 and is generally inferred to be given by Fig. 2 under the assumption that the three basal oxygens are bridging back into the solid and the orbital of the unpaired spin is projecting into the vacuum. By comparing the experimental powder spectrum of the E_s' central line with computer simulated line shapes, Hochstrasser and Antonini inferred the g tensor to be perfectly axial—a result consistent with the C_{3v} symmetry of the structure of Fig. 2. The larger measured value for the "strong" hf splitting ($A_{\text{iso}} \approx 465$ G) can be interpreted as indicating[12] that the bond angle ρ is approximately 1° larger in the case of E_s' relative to the bulk E' centers.

There is evidence from optical spectra that both the E_1' and E_2' defects exist in irradiated glassy silica and that they can be interconverted by various bleaching and annealing treatments.[1] Nevertheless, the crystallographic distinctions between the E_1' and E_2' species noted above cannot be made in a glass and, moreover, the weak proton hfs characteristic of the E_2' center has never been resolved (or deconvoluted) from the angularly averaged glass spectra. In fact, earlier studies of bulk E' defects in glassy SiO_2 have concentrated on the g tensor[1] and "strong" hfs[12] as the primary means of identification and characterization.

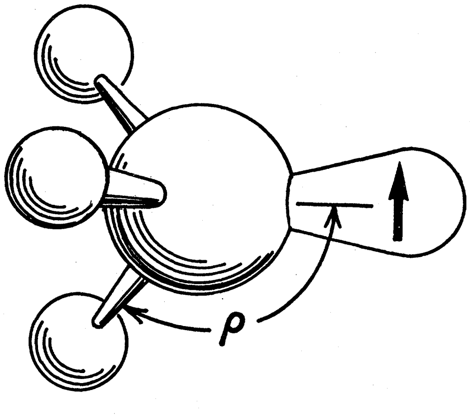

FIG. 2. Less specific E'-center model, as inferred only from ^{17}O and "strong" ^{29}Si hfs data. Large sphere represents a silicon; smaller spheres are oxygens. A "balloon" encloses the region of high unpaired spin density (indicated by an arrow). The angle ρ is approximately the tetrahedral angle (109.47°) but varies ~ ±1° depending on the influence of longer-range order (Ref. 12).

Against this background, Shendrik and Yudin[13] recently raised the possibility that both the "strong" and "weak" hfs of the E' center in both glassy and crystalline forms of SiO_2 may be due to protons present as inadvertant impurities, rather than to ^{29}Si as generally believed. However, in Paper I[14] of this series it was firmly established that the 420-G doublet seen in glassy silica (and by inference the 410-G "strong" hfs seen in α quartz) is definitely the primary ^{29}Si hfs of the E' center as originally assumed.[15] It was thence inferred[14] that the structure of this defect in both the crystalline and glassy polymorphs of SiO_2 embodied the common characteristic of an unpaired spin completely localized in the dangling tetrahedral orbital of a silicon which is pyramidally bonded to three oxygens in the crystal or glass network (Fig. 2). The question of whether or not these three basal oxygens are chemically equivalent and further questions regarding next-nearest-neighbor atomic arrangements were left unaddressed at that time.

In parallel with the experimentally oriented work described above, a number of theorists had begun to approach the problem of defects in amorphous SiO_2 in a broad general way by examining the consequences of various "new" bonding configurations which might conceivably be possible only in the vitreous state. In particular, some of the ideas of Mott and co-workers[16] and of Kastner *et al.*[17] originally advanced in the context of the chalcogenide glasses were adapted in several different ways to the case of glassy silica. Greaves,[18] for example, hypothesized that the concept of vacancies and interstitials, familiar from the study of crystals, need not pertain to glasses.[19] He believed that the basic defects in glassy silica prior to irradiation are the isolated three-coordinated silicon and the nonbridging (singly bonded) oxygen. Greaves reasoned, however, that these structures might lower their energies by distorting in such a way as to form new bonds with other oxygens which were already fully coordinated (bridging oxygens). In this scheme, Greaves visualized the bulk E' center as the structure illustrated in Fig. 1(b), where the defect silicon is "partially bonded" to an otherwise normal bridging oxygen which shares the unpaired spin to some significant degree. By contrast, Lucovsky[20] proposed criteria which led to a model for the E' center as an unpaired spin localized on a silicon bonded to one nonbridging and two bridging oxygens and in the immediate neighborhood of a fourth oxygen which according to this author had been three coordinated and bonded to the defect silicon prior to electron trapping [Fig. 1(c)].

The observed magnitudes of the primary ^{29}Si hfs were previously invoked to support the notation that the structures of the E' centers in α quartz and fused silica are essentially identical [i.e., both take the form of Fig. 1(a)].[12,14] However, the primary hfs data alone do not clearly eliminate the kinds of models proposed by Greaves[18] and Lucovsky.[20] Moreover, several puzzles and questions regarding details of the Fiegl-Fowler-Yip model have remained unanswered, as alluded in the opening paragraphs. Accordingly, a new series of experiments have been devised and carried out with the objective of defining more precisely the structure of the E' center in glassy silica. These experiments, described below, take advantage of fused silica samples enriched in ^{17}O, as well as samples enriched (or depleted) in ^{29}Si.

II. EXPERIMENTAL

Samples for the present study included: (i) high-purity commerical silicas containing ~1200 ppm OH (Suprasil 1 and 2) and <5 ppm OH (Suprasil W1 and Corning 7943) in both powder and 6-mm-diameter rod forms; (ii) glassy silica samples of diverse ^{29}Si:^{28}Si ratios as described previously[14]; (iii) glass samples enriched to 18 and 36 at.% ^{17}O by reacting ^{17}O-enriched water with $SiCl_4$ and fusing the resulting precipitate[21]; and (iv) powdered Suprasil samples wherein impurity protons were exchanged with deuterons.[22] Also investigated was one small sample comprising a number of hydrothermally grown, submillimeter single crystals[23] of α quartz enriched to ~30 at.% ^{17}O. All samples were irradiated with ^{60}Co γ rays to total doses ranging from 3×10^7 to 8×10^8 rads (Si). ESR spectra were obtained at *X*-band (~9.1 GHz) and *Ka*-band (~35 GHz) frequencies on a Varian E-9 spectrometer employing 100-kHz field modulation. Most measurements to be discussed were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. ^{17}O superhyperfine structure

Figure 3 compares the E' center spectra of the ^{17}O-enriched samples with a spectrum typical of high-purity fused silicas containing ^{17}O in its natural abundance (3.7×10^{-2} at.%). The considerably broadened "wings" noted for the isotopically enriched samples were found to be essentially independent of temperature, spin concentration, and microwave power. It is thus inferred that these wings must be due to unresolved superhyperfine (shf) interactions with ^{17}O ($I = \frac{5}{2}$) or with some impurity in the ^{17}O-enriched water which was used as a starting material. Since a small aluminum impurity concentration had been shown[21] to be present in these samples in proportion to the degree of ^{17}O enrichment, the latter possibility must first be considered. To begin with, it should be noted that the literature is rife with ESR studies of defect centers in Al-doped α quartz and fused silica,[24,25] and in no case has there been reported a defect with g values close to those of the E' center also having ^{27}Al hfs ~2 G—as would be necessary to account for the results of Fig. 3 in terms of an Al impurity center. Indeed, Brower[25] has

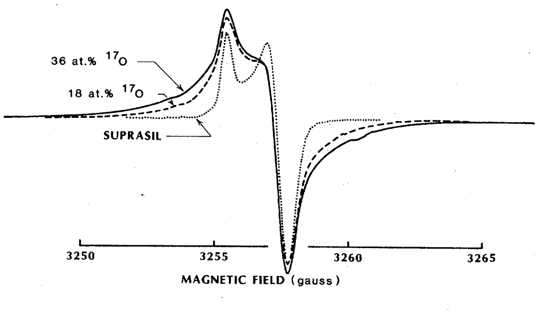

FIG. 3. *X*-band ESR absorption spectra of E' centers in high-purity commercial silica (exemplified by Suprasil, dotted curve) and in silica samples enriched to 18 and 36% in the ^{17}O isotope (dashed and unbroken curves, respectively).

reported the Al E' center in Al-doped silica to exhibit ^{27}Al hfs splitting ~400 G. Moreover, irradiated glassy silica samples[26] deliberately doped with 0.5 at. % Al were found in the present study to exhibit Si E' center spectra differing only subtly from that of Suprasil and in no way approximating those of the ^{17}O-enriched samples. Thus, there is seen to be a strong *a priori* case for presuming that the spectral broadening of the E' center resonance in the ^{17}O-enriched specimens is wholely due to unresolved shf interactions with that nucleus.

Accepting this premise, it becomes possible by spectral analysis to draw some inferences regarding the natures of the E' center's nearest oxygen neighbors in glassy SiO_2. For example, if the E' center has three chemically equivalent oxygen neighbors (as in the Feigl-Fowler-Yip theory), the distribution of oxygen isotopes among these three oxygens would be given by Table I for the two levels of isotopic enrichment employed in this experiment. Figure 4 shows a computer simulation[27] of the spectrum of the 36 at. %-enriched sample assuming three equivalent oxygens and using the probability factors listed in Table I as a constraint.[28] By a cut-and-try procedure the fit was gradually improved by varying the distribution of isotropic shf coupling constants a assigned to the magnetic oxygen nuclei. It should be noted that the distribution $P(a)$ which finally optimized the fit (Fig. 4, inset) is characterized by a mean value and halfwidth which are both large with respect to the dipole-dipole interaction calculated according to

$$b_{\mathrm{calc}} = \tfrac{2}{5} g_N \mu_N \langle r^{-3} \rangle \ , \qquad (1)$$

where g_N is the nuclear g factor (for ^{17}O $g_N = -0.7573$), μ_N is the nuclear magneton, and r^{-3} was estimated from the charge-density distribution of the E' center calculated by Gobsch *et al.*[5] To the extent that the wave function of the unpaired spin in Fig. 2 is expected to have no overlap with the three basal oxygens, neglect of anisotropic hfs in the simulation is therefore justified.

TABLE I. Statistical weights associated with finding 0, 1, 2, or 3 ^{17}O nuclei occupying the three equivalent oxygen sites illustrated in Fig. 2 for two different isotopic enrichments.

Isotopic distribution of basal oxygens	Probability 18 at. % ^{17}O	Probability 36 at. % ^{17}O
all ^{16}O	0.551	0.262
one ^{17}O	0.363	0.442
two ^{17}O	0.080	0.249
all ^{17}O	0.006	0.047

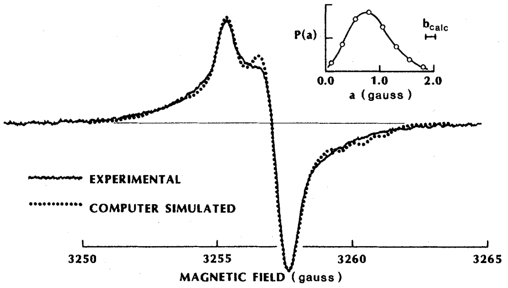

FIG. 4. X-band ESR absorption spectrum of E' centers in glassy silica enriched to 36 at. % in the ^{17}O isotope. Unbroken curve is the experimental first-derivative spectrum and the dotted curve is a computer simulation accomplished under the model assumption that the unpaired spin undergoes a hyperfine interaction with ^{17}O nuclei at three chemically equivalent sites. Inset shows distribution of isotropic hf coupling constants a employed to achieve the illustrated simulation. Also indicated is the calculated dipole-dipole coupling b_{calc} between the electron spin and the ^{17}O nuclei.

The success of the simulation of Fig. 4 (and of a corresponding simulation for the 18 at. %-enriched sample) is strong support for the model assumption that the E' undergoes shf interactions with three nearly identical oxygens. Simulations assuming interactions with ^{17}O nuclei at just two or one neighboring sites do not exhibit sufficient intensity in the "wings." This is easily understandable when it is recognized from Table I that, for 36 at. % enrichment, nearly 74% of the intensity is subject to ^{17}O shf splittings in the three-equivalent-oxygen case, whereas only 36% of the intensity would be subject to such splittings were the primary interaction with a single oxygen. Thus, the model proposed by Greaves [Fig. 1(b)], wherein the unpaired electron must spend a considerable portion of its time on a single oxygen, is essentially eliminated. This model would also be ruled out by the small magnitude of the observed splitting ($a_{\mathrm{meas}}/a_{\mathrm{atomic}} \approx 5 \times 10^{-4}$).[29] In the present context, it is appropriate to point out that the intensity of the E' line, determined by exact numerical integration, was the same (within ±10% error) in the ^{17}O-enriched silicas as it was in a sample of Suprasil 2 exposed to the same radiation dose. This last finding, coupled with the absence of any additional structure in wide-sweep traces obtained at high gain, eliminates the possible existence of ^{17}O hf splittings of a much larger magnitude than those simulated in Fig. 4. On the other hand, the simulation of Fig. 4 does not prove that all three oxygens are *exactly* equivalent [owing to the considerable breadth of the $P(a)$ distribution in Fig. 4], nor does it eliminate the possibility of a weaker interaction with a fourth oxygen. Therefore, it is desirable to develop other means for evaluating the viability of the Lucovksy model of Fig. 1(c) (see Sec. III D, below).

A small polycrystalline sample of ^{17}O-enriched α quartz was also investigated as an additional test of the hypothesis that the hfs simulated in Fig. 4 is due to ^{17}O. The *X*-band spectrum of the crystalline sample indeed bore a closer resemblance to that of Fig. 4 than to the spectrum of Suprasil, but the signal-to-noise ratio was rather low, owing to the smaller number of defects formed in the crystalline vis-à-vis the glassy material as well as to the poor cavity filling factor. This unsatisfying result became the motivation for a series of measurements at *Ka* band, where the filling factor was nearly ideal. It was found, however, that absorption mode measurements at *Ka* band were impossible on the Varian 35-GHz bridge due to inadvertent cross talk with the rapid passage dispersion signal. Consequently, spectra were obtained in the high power dispersion mode, leading to line shapes which appeared to resemble the undifferentiated absorption curves.[30] It can be seen in Fig. 5 that the *Ka*-band dispersion mode spectrum of Suprasil 2 (heavy, unbroken curve) is closely replicated by a no-adjustable-parameters simulation of the E' center absorption curve (dots) using the g-value distributions estimated for glassy silica in Ref. 14.

It is evident in Fig. 5 that the E' center spectrum of ^{17}O-enriched α quartz is subjected to shf splittings of the same order of magnitude as those observed for the isotopically enriched glasses. Although no attempt was made to simulate the hf structure apparent in these dispersion mode spectra, the splitting in the α quartz case appears to be approximately two times larger than the mean splitting in the glass case. It is not unreasonable to expect different mean ^{17}O hf coupling constants for different polymorphs of SiO_2, since the mean bond angle ρ of Fig. 2 is inferred[12] to be ~0.25° smaller for α quartz than for glassy silica. It should be noted further that there is an estimable distribution of bond angles in the glass (half-width ~0.7°)[12] which is mimicked by a distribution in ^{17}O hf constants $P(a)$ (Fig. 4, inset). In particular, $P(a)$ has a finite amplitude at values of $a(^{17}\mathrm{O})$ which exceed the mean value by a factor of 2. Thus, leaving aside questions regarding the physics of the implied relationship between bond angle and ^{17}O hyperfine coupling, it appears that the E' center spectrum of ^{17}O-enriched α quartz is empirically consistent with the spectra of glassy silica samples similarly enriched. This finding essentially completes the proof that the observed "wings" which characterize the E' spectra of the ^{17}O-enriched specimens indeed arise from ^{17}O shf interactions rather than impurity effects, since many impurities (other than Al) which might have been incorporated in the glass are generally rejected during crystal growth.[31]

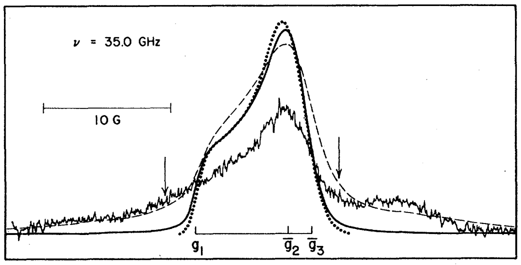

FIG. 5. *Ka*-band ESR dispersion mode spectra of E' centers in Suprasil 2 (heavy, unbroken curve), glassy silica enriched to 36 at.% ^{17}O (dashed curve), and a polycrystalline α-quartz sample enriched to 30 at.% ^{17}O (noisy trace). Dotted curve is a computer simulation of the E' center absorption spectrum associated with nonmagnetic silicon and oxygen nuclei, using the g value distributions estimated in Ref. 14. Field positions corresponding to the principal components of the E' g matrix in glass are indicated by a comb. Arrows locate the mean extent of the $m_I = \pm\frac{5}{2}$ ^{17}O hf lines in the glass spectrum, based on the computer simulation of Fig. 4.

It should be remarked in passing that several attempts, each unsuccessful, were made to fit the spectrum of Fig. 4 with more symmetrical $P(a)$ functions having finite values at $a = 0$. One thereby infers that virtually all E' centers in the glass are characterized by ^{17}O shf splittings large enough to be measured.

B. "Weak" hfs: protons

Shendrik and Yudin[13] published what may be the first report of the "weak" satellite structure (peak-to-peak separation 12.6 G) centered on the ^{28,30}Si E' center resonance in glassy silica. Although the latter authors mentioned observing this apparent doublet structure only in glasses which had been heat treated in H_2 prior to irradiation, Paper I[14] noted its occurrence in a wide range of untreated, but carefully outgassed silica samples containing either 5 or 0 at.% ^{29}Si. On the basis of the last-mentioned observation Paper I was in concurrence with Shendrik and Yudin that the origin of this "weak" hfs must be primarily related to a proton impurity in vitreous SiO_2. However, since the believed existence of "weak" ^{29}Si hfs in α quartz has had a major impact on the current theory of the E' center (see Sec. I), the E' center spectrum of glassy silica was reexamined in careful detail in the present study for any evidence that some fraction of the 12.6-G structure may after all be due to ^{29}Si hfs. [It should be noted that trial computer simulations of the "12.6-G" satellite structure of Fig. 6(a) have shown that, if it is a doublet, it is characterized[32] by an hf splitting $a \approx 8$ G—a value essentially identical to the "weak" hfs ascribed to ^{29}Si in α quartz.[2]]

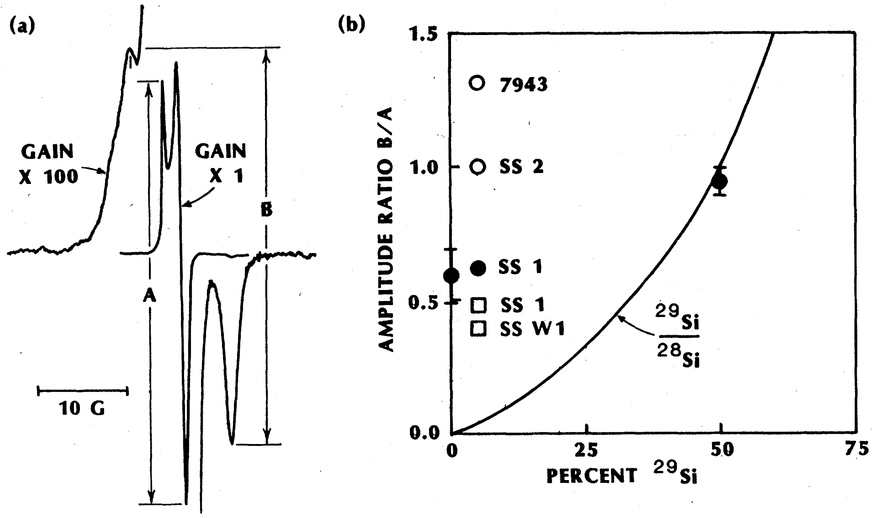

FIG. 6. (a) *X*-band ESR absorption spectrum of E' centers in an irradiated fused silica, showing "weak" (12.6-G) satellite structure at high spectrometer gain. (b) A plot of the ratio of the spectral amplitudes defined in (a) vs the isotopic abundance of ^{29}Si in the samples. Circles denote powdered samples, while squares represent data for 6-mm-diameter rods. Filled circles pertain to a suite of samples subjected to outgassing at 1000 °C prior to irradiation (Ref. 14). Curve in (b) represents the theoretical dependence of B/A upon isotopic abundance under the assumption that the "weak" satellite structure is due solely to ^{29}Si shf.

Many of the significant results of the present study vis-à-vis the "weak" hfs in glassy silica are portrayed in Fig. 6(b). Here, it can be seen that the ratio of the amplitude B of the 12.6-G structure to the amplitude A of the E' central line is almost independent of ^{29}Si isotopic abundance in the range 0–50 at.%. This behavior is in dramatic contrast to that predicted in the event that the satellite structure were due solely to ^{29}Si [curve in Fig. 6(b)]. It is further seen in Fig. 6(b) that the amplitude ratio for fused silicas containing ^{29}Si in its natural abundance varies widely among commercial glasses of different origins. Finally, it was noted that the ratio B/A for powdered Suprasil 2 was reduced by 25% in a sample where the protons were partially exchanged for deuterons.[33] These various observations confirm that a major fraction of the 12.6-G structure must be due to protons associated with a few percent of the E' sites.

The filled circles in Fig. 6(b) exhibit a trend which could be explained by assuming that a minor fraction of the 12.6-G structure in the outgassed samples is due to "weak" ^{29}Si hfs of the E' center. Were this the case, however, it is easily demonstrated by computer simulation that SiO_2 samples enriched to 95 at.% ^{29}Si should display an 8-G doublet (or a 16-G triplet in the case of *two equivalent* next-nearest-neighbor silicons) in place of the usual $^{28,30}Si$ E' central line. But contrary to these predictions, examination of two separate 95 at.%-enriched samples[14] at high gain revealed in each case only the usual E' central line flanked by relatively weak "wings." The high-power dispersion mode spectra of Fig. 7 show clearly that the weak "wing" structure associated with the E' central line in ^{29}Si-enriched samples remains entirely too weak (relative to the central line) to be interpreted as arising from ^{29}Si shfs with $a \approx 8$ G. It is noteworthy in Fig. 7, however, that the mean splitting of the "wings" outside of the

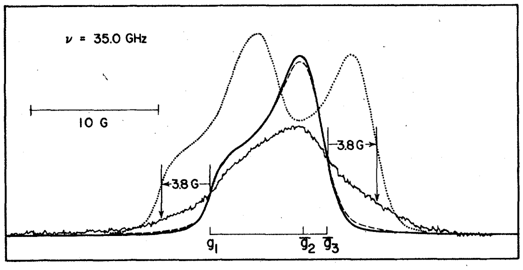

FIG. 7. *Ka*-band ESR dispersion mode spectra of E' centers in glassy silica containing 0 at.% ^{29}Si (heavy, unbroken curve), 50 at.% ^{29}Si (dashed curve), and 95 at.% ^{29}Si (noisy trace). Dotted curve is a hypothetical spectrum of an E' center undergoing an hf interaction with a 95 at.%-abundant spin-$\frac{1}{2}$ nucleus characterized by $a = 8$ G. Arrows locate the approximate centers of low-intensity "wings" associated with the E'-center spectrum in silica enriched to 95 at.% ^{29}Si. The separation between these "wings" and the maximum-slope points of the 0 at.% ^{29}Si spectrum is ~3.8 G, the Larmor frequency of the ^{29}Si nucleus in the applied field of 12.5 kG. Field positions corresponding to the principal components of the E' g matrix in glass are indicated by a comb.

maximum-slope points of the 0 at.% ^{29}Si spectrum is approximately equal to $h\nu_L/2\mu_B = 3.8$ G, where μ_B is the Bohr magneton and ν_L is the Larmor frequency of the ^{29}Si nucleus in the applied field of 12.5 kG (10.57 MHz). As discussed by Weil and Anderson,[34] quasiforbidden transitions (simultaneous electron and nuclear-spin flips) could be responsible for such "wing" structure in the event that the actual ^{29}Si shf coupling constant were substantially smaller than $h\nu_L$. This possibility is essentially confirmed in the following section by an analysis of the X-band spectra of the 95 at.% ^{29}Si-enriched samples. The conclusion is therefore compelled that the 12.6-G "weak" hfs is due entirely to a small fraction[35] of the E' sites incorporating a proton. The slight increase of B/A with increasing ^{29}Si content seen in Fig. 6(b), if real, is likely to be a consequence of the broadening of the central line due to the "very weak" ^{29}Si hfs *(vide infra)*.

C. ^{29}Si "very weak" hfs

In addition to the "strong" and "weak" hfs described above, Weeks[6] has reported "very weak" hf doublets having splittings approximately 1.2 and 0.6 G for the E_1' center and 1.1, 0.9, and 0.4 G for the E_2' center when the magnetic field was applied parallel to the c axis. While this "very weak" structure has been generally ascribed[2,4–6] to ^{29}Si nuclei in near-neighbor positions, there has been no agreement among authors regarding specifically which silicon sites are responsible. The E' central line spectra for the glass samples enriched to 95 at.% ^{29}Si should bear strongly on this question since each near-neighbor silicon position now has a 95% probability of being occupied by a ^{29}Si. For this reason, extreme care was taken to assure that the X-band spectra of Fig. 8 were reproducible and undistorted by modulation or passage effects.[36] For the same reason, considerable effort was devoted to computer simulating this line shape under various model assumptions.

More than a dozen trial simulations were carried out, each employing as a constraint the g value distributions previously determined[14] for the E_1' center in outgassed, irradiated Suprasil 1 (see Fig. 9). The simulation for the Suprasil spectrum itself involved using a Gaussian convolution function characterized by a second moment $\mu_1 = 0.15$ G attributed[14] entirely to a distribution in g_1, the principal g value closest to that of the free electron (distributions in the other two principal g values were incorporated explicitly). Since this same source of inhomogeneous broadening is presumably present in the enriched samples as well, the convolution function characterized by $\mu_t = 0.30$ G used in achieving the dotted simulation of Fig. 8(a) reflects an added source of broadening $\mu_2 = (\mu_t^2 - \mu_1^2)^{1/2} = 0.26$ G. If this added broadening is due to "very weak" ^{29}Si shfs with a single shell of equivalent silicons, then it is given by[37]

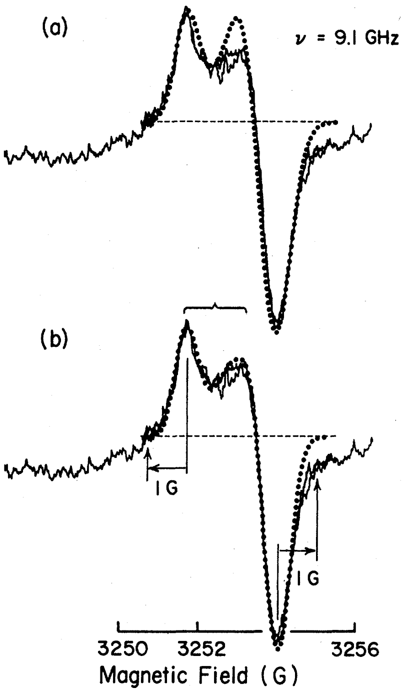

FIG. 8. X-band ESR absorption spectra of E' centers primarily localized on nonmagnetic silicon isotopes in a glass enriched to 95 at.% ^{29}Si. Dotted computer simulation in (a) was achieved using the g value distributions derived in Ref. 14 and a Gaussian convolution function characterized by a second moment $\mu_t = 0.30$ G. Dotted simulation in (b) took explicit account of a "very weak" hf interaction with a single ^{29}Si nucleus assuming the coupling constants to be correlated with the inverse third power of the g shift (see text); a Gaussian convolution function was employed characterized by $\mu_t = 0.20$ G. Experimental spectra in (a) and (b) are identical. Arrows indicate the apparent existence of "wings," split away from the main resonance by about 1 G, the Larmor frequency of the ^{29}Si nucleus in an applied field of 3.25 kG.

$$\mu_2 = \bar{A}\sqrt{I(I+1)N\xi/3} = \tfrac{1}{2}\bar{A}\sqrt{N\xi} \ , \qquad (2)$$

where $\bar{A}$ is the mean shf splitting arising from ^{29}Si nuclei of isotopic abundance ξ in N equivalent sites. If, for example, it is assumed that $N = 3$, the value of μ_2 inferred from the simulation of Fig. 8(a) yields $\bar{A} = 0.31$ G. Thus, if the dotted curve of Fig. 8(a) were regarded as an adequate simulation of the experimental spectrum, it might be suggested that the E' center in glassy SiO$_2$ interacts with ^{29}Si nuclei in three next-nearest-neighbor positions by means of a superexchange mechanism[2] acting through the three basal oxygens of Fig. 2, with mean isotropic splittings $a \approx 0.3$ G. Superexchange must be invoked here since the dipole-dipole interaction with the same silicons is calculated from Eq. (1) to be only $b \approx 0.05$ G.

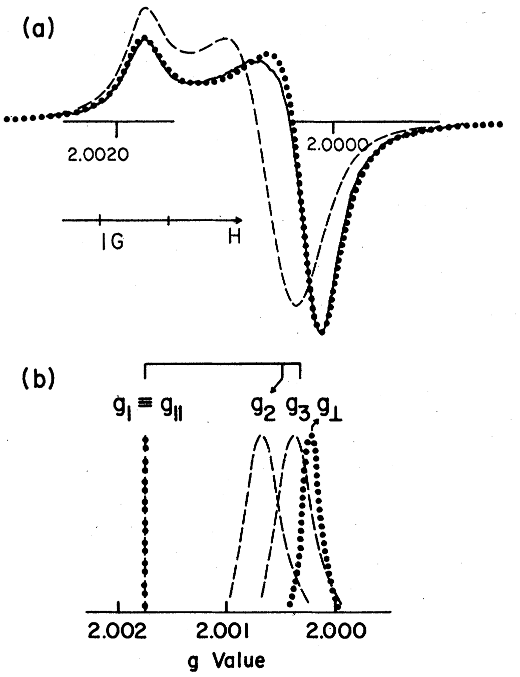

FIG. 9. X-band ESR absorption spectra of surface and bulk E' centers. Unbroken curve in (a) is a typical experimental spectrum of surface E' centers formed by crushing either α-quartz or fused silica under ultra-high vacuum (after Ref. 11). Dotted curve in (a) is a computer simulation of the E_s' spectrum assuming an axially symmetric g matrix and using the dotted distribution in parameters indicated in (b). Dashed curve in (a) is a simulation of the spectrum of bulk E' centers in fused silica using the g value distributions [dashed curves in (b)] derived in Ref. 14. For comparison purposes it was assumed that g_1(bulk) $= g_\parallel$ (surface), and identical Lorentzian convolution functions were used in both simulations. For reference, the comb in (b) represents the g matrix of the E_1' center in α quartz after Ref. 2.

On the other hand, one may ask the question whether part of the unresolved broadening in the experimental spectra of Fig. 8 might be due to an interaction with a ^{29}Si nucleus at the position of the second (relaxed) silicon in the model of Fig. 1(a). This possibility was tested by carrying out a number of simulations wherein a "very weak" hf doublet was included explicitly. Use of discrete splittings <0.3 G yielded simulations which were virtually indistinguishable from that of Fig. 8(a). Larger discrete splittings resulted decidedly degraded fits. However, it was found that improved fits could be obtained by assuming a distribution of splittings positively correlated with the inverse third power of the principal g shifts, i.e., $A \propto (g_e - g_3)^{-3}$, where g_e is the free-electron g value and the distribution in g_3 values $P(g_3)$ is taken to be that shown in Fig. 9(b). The result of one such simulation is given by the dotted curve in Fig. 8(b), where the region of improved agreement with experiment is indicated by a bracket.

The improved fit of Fig. 8(b) vis-à-vis Fig. 8(a) supports the possibility that the second silicon of Fig. 1(a) could be contributory to the "very weak" shfs broadening of the E' central line in ^{29}Si-enriched silica. Of course, conclusive proof for such a postulate is still lacking. Significantly, however, the simulations of Fig. 8 place a stringent upper limit of ~ 1.3 G on the maximum shf splitting due to the second silicon. Thus, in the event that the model of Fig. 1(a) is indeed germane to the E' center in glassy silica *(vide infra)*, the overlap of the E' charge cloud on the second silicon is deduced to be substantially smaller than implied by recent theoretical calculations ($a_{\text{calc}} \sim 5-10$ G and $b_{\text{calc}} \sim 1-5$ G).[4,5]

It should be noted that the computer fits of Fig. 8 are both hindered by a tilted base line and both fail to reproduce a weak "wing" structure extending ~ 1 G to the high- and low-field sides of the principal line. The base-line effect has been shown to be due to a broad underlying resonance centered at a higher field in this particular ^{29}Si-enriched sample and hence can be disregarded. On the other hand, the "wings" appear to be inate features of the resonance which cannot be computer simulated under any reasonable model assumption when the spin Hamiltonian is taken to comprise only the electron-Zeeman and ^{29}Si-hyperfine terms. Since the Larmor frequency of the ^{29}Si nucleus in an applied field ~ 3250 G is given by $h\nu_L/2\mu_B \approx 1.0$ G, it is suggested that the "wings" observed at 9.1 GHz, like the broader "wings" seen at 35 GHz (Sec. III B, above) arise from quasiforbidden transitions which can be shown to occur in these relative field positions when account is taken of the direct interaction of the nucleus with the applied magnetic field.[34]

D. g-tensor considerations

The hfs data discussed above place definite constraints on any structural models for the E' center in glassy silica, but they still do not prove that the correct model for the glass must be identical with the correct model for α quartz. The ambiguity, of course, lies with the quartz data: It is not known for certain whether the so-called "weak" hf splittings in α quartz are due to ^{29}Si, as long supposed, or whether they are due to protons as demonstrated in Sec. III B to be the case in the glasses. Ultimately, it will be necessary to investigate α-quartz samples enriched with ^{29}Si in order to resolve this question. In the meantime, it appears possible to bypass the hf data and draw some tentative conclusions by comparing the g tensors for the E' centers in glassy silica and α quartz.

It can be recalled from Paper I[14] that the computer simulation of the E' central line in pure glassy silica yielded principal-axis g values which, though slightly distributed due to vitreous disorder, averaged to values very close to those reported for α quartz. This agreement extended even to the orthorhombic components of the respective matrices. It is crucial to note at this juncture the fact that E_s' centers comprising dangling silicon bonds on pristine silica or α-quartz surfaces were believed to be characterized by perfect axial symmetry in their g matrices.[11] This belief was rechecked in the present study as illustrated in Fig. 9. The experimental E_s' spectrum of this figure, together with its g value scale, was taken directly from the work of Hochstrasser and Antonini[11] and the dotted computer simulation was achieved under the assumption of axial symmetry using the illustrated distribution of $g_\perp$ values. For comparison, the dashed curve is a computer simulation of the bulk E_1' center spectrum in glassy silica at the same frequency and scan rate using the g values[38] derived in Ref. 14. To make the comparison meaningful, the same Lorentzian convolution linewidth was used in both cases (even though a substantially narrower convolution function is obtained when fitting the bulk glass spectrum[14]). It can be seen clearly in Fig. 9 that the spectra of surface and bulk E' centers are distinctively different even when convoluted by the same broad Lorentzian function. In fact, when one undertakes actual computer simulations it is quickly apparent that the orthorhombic component of the g matrix which characterizes the bulk E' center in both glassy and α-quartz forms of SiO_2 is substantially smaller, if not absent, in the case of the surface E' center formed by crushing either of these polymorphs *in vacuo*.

It seems safe to conclude from these observations that the orthorhombic component in the E'-center g matrix arises from that part of the crystal or glass structure which distinguishes a bulk defect from a defect which exists at the solid-vacuum interface. If it is assumed (based on the similarity of the ^{17}O and "strong" ^{29}Si hf interactions) that all E' centers have in common the basic structure illustrated in Fig. 2, it must be concluded that the orthorhombic component is imposed by some off-axis atomic arrangement which exists immediately to the right of the charge cloud of the unpaired spin in Fig. 2. According to the generally accepted Feigl-Fowler-Yip theory[3,4] this atomic arrangement is the relaxed "second silicon" as represented by Fig. 1(a) in the case of α quartz.

Gobsch *et al.*[5] performed a series of theoretical calculations of the E'-center g matrix under the constraints of the Feigl-Fowler-Yip model. These authors found approximately the correct orthorhombic component when their calculations were carried out for the α-quartz lattice, but they obtained an axial g matrix for idealized β cristobalite wherein the second silicon is coaxial with the defect charge cloud. These results seem to provide a validation of the Feigl-Fowler-Yip model in general and of the explanation of the origin of the orthorhombic component of the g matrix in particular.

It would be a rather improbable coincidence if a completely different structural model such as that of Fig. 1(c) would yield a g matrix nearly identical with that of the oxygen vacancy of Fig. 1(a). In any event, the model of Fig. 1(c) is incompatible with the crystal structure of α quartz so, even if the calculations of Gobsch *et al.*[5] are discounted, Lucovsky's model[20] cannot be the correct one for E_1' center in this crystalline polymorph. The virtually identical g matrices determined for E' centers in α quartz and fused silica (see Fig. 9 and Ref. 38) strongly imply that these defects are essentially identical in both polymorphs as regards to their near-neighbor atomic arrangement to the right of the dangling orbital in Fig. 2. All available data and theoretical calculations support the model of Fig. 1(a) as giving the best description of these arrangements. Thus, the concept of an oxygen vacancy would seem to have the same validity and implications in glassy silica as it does in the crystalline polymorphs of SiO_2.

IV. CONCLUSIONS AND CAVEATS

It has been shown that the E' center in silica glass undergoes a hyperfine interaction with ^{17}O nuclei statistically occupying three essentially equivalent near-neighbor sites. This finding, coupled with previous knowledge of the "strong" ^{29}Si hf interaction,[2,12,14] leads to the conclusion that E' centers in both glassy and α-quartz forms of SiO_2 are characterized by an unpaired spin in a dangling hybrid orbital of a silicon bonded to three oxygens in the glass or crystal network. In the α-quartz lattice, this orbital has been believed to project into an oxygen vacancy and to undergo a "weak" hf interaction[2] ($a \approx 8$ G) with the opposing, asymmetrically relaxed[3-5] three-coordinated silicon. This explanation of the origin of these particular "weak" hf lines observed[2] in α quartz has never been verified by ^{29}Si enrichment experiments, however. The origin of a *second set* of "weak" hf lines associated with the E' center in α quartz has neither been verified nor explained theoretically. The present study has confirmed an earlier suggestion[13] that similar "weak" hfs ($a \approx 8$ G) observed in glassy silica is due to impurity protons, rather than ^{29}Si nuclei. The spectra of $^{28,30}Si$ E' centers in glassy SiO_2 enriched to 95 at.% ^{29}Si reveal the presence of unresolved "very weak" ^{29}Si hfs ($a \approx 0.3-1.2$ G) similar in magnitude to structure likewise ascribed to ^{29}Si nuclei in α-quartz.[6] In principle, this "very weak" hfs could be due to the asymmetrically-relaxed, "second silicon" if oxygen vacancy model for the E' center is equally valid in silica glass and α quartz.

The nearly identical orthorhombic components of the bulk-E' center g matrices in these two polymorphs, when compared to the axial g matrix for the surface E' center,[11] are cited above as compelling evidence that the oxygen-vacancy model of Feigl, Fowler, and Yip[3,4] should be accepted for glassy fused silica, just as it has been in the case of α quartz. A corollary of this conclusion is that the so-called "weak" hfs of the E' center in α quartz must be due to impurity protons. The latter inference confounds earlier theoretical calculations of one of the "weak" doublets but explains the previous inability of theorists to calculate the second pair of "weak" hf lines.[3-5] Of course, it remains desirable to test this suggestion by studies of α-quartz samples enriched in ^{29}Si.

The number density of E' centers stable at room temperature in the glasses of the present study generally ranged between 10^{16} and 10^{17} g^{-1} (see Ref. 14 for further discussion of spin concentrations). If there exist any other paramagnetic E'-center variants ("wrong bonds," "new bonds," or "valence alteration pairs") in these samples, their number densities must be $<10^{15}-10^{16}$ g^{-1}, since otherwise their effect would have been manifest as anomalies in the data. It should be cautioned, however, that many of the oxygen vacancies inferred to be the E' hole-trapping sites may have resulted from displacements induced by the high doses of 1.5-MeV γ rays administered in this study.[39] The possible existence of some isolated, positively charged three-coordinated silicons in unirradiated glassy silica is therefore not disproved. Rather, upper limits have been placed on the number density of E'-type defects which may result from the trapping of single electrons on such structures.

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[1] R. A. Weeks, J. Appl. Phys. 27, 1376 (1956); C. M. Nelson and R. A. Weeks, J. Am. Ceram. Soc. 43, 396 (1960); R. A. Weeks and C. M. Nelson, *ibid.* 43, 399 (1960); J. Appl. Phys. 31, 1555 (1960).

[2] R. H. Silsbee, J. Appl. Phys. 32, 1459 (1961).

[3] F. J. Feigl, W. B. Fowler, and K. L. Yip, Solid State Commun. 14, 225 (1974).

[4] K. L. Yip and W. B. Fowler, Phys. Rev. B 11, 2327 (1975).

[5] G. Gobsch, H. Haberlandt, H. -J. Weckner, and J. Reinhold, Phys. Status Solidi 90, 309 (1978).

[6] R. A. Weeks, Phys. Rev. 130, 570 (1963).

[7] F. J. Feigl and J. H. Anderson, J. Phys. Chem. Solids 31, 575 (1970).

[8] G. S. Smith and L. E. Alexander, Acta Crystallogr. 16, 462 (1963).

[9] L. E. Halliburton, B. D. Perlson, R. A. Weeks, J. A. Weil, and M. C. Wintersgill, Solid State Commun. 30, 575 (1979).

[10] L. E. Halliburton and J. A. Weil (private communication).

[11] G. Hochstrasser and J. F. Antonini, Surf. Sci. 32, 644 (1972).

[12] D. L. Griscom, E. J. Friebele, and G. H. Sigel, Jr., Solid State Commun. 15, 479 (1974).

[13] A. V. Shendrik and D. M. Yudin, Phys. Status Solidi B 85, 343 (1978).

[14] D. L. Griscom, Phys. Rev. B 20, 1823 (1979).

[15] Further discussion bearing on this issue has appeared recently [see, K. L. Brower and J. Vitko, Jr., Phys. Status Solidi B 95, K141 (1979); A. V. Shendrik and D. M. Yudin, *ibid.* 95, K145 (1979)].

[16] N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. 32, 961 (1975); R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975); N. F. Mott and R. A. Street, Philos. Mag. 36, 33 (1977).

[17] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. 37, 1504 (1976); M. Kastner, Philos. Mag. B 37, 127 (1978); M. Kastner and H. Fritzsche, *ibid.* 37, 199 (1978); H. Fritzsche and M. Kastner, *ibid.* 37, 285 (1978).

[18] G. N. Greaves, J. Non-Cryst. Solids 32, 295 (1979).

[19] Recently, data and arguments have been mustered which conflict with Greaves' suggestion. Namely, the demonstrated existence of the peroxy radical defect in fused silica supports the notion that oxygen vacancies and interstitials (in the form of O_2^{2-} crowdions) are valid concepts in glassy SiO_2. [See, E. J. Friebele, D. L. Griscom, M. Stapelbroek, and R. A. Weeks, Phys. Rev. Lett. 42, 1346 (1979).]

[20] G. Lucovsky, Philos. Mag. B 41, 457 (1980).

[21] Details of sample preparation and the results of other experiments performed on these samples are provided in M. Stapelbroek, D. L. Griscom, E. J. Friebele, and G. H. Sigel, Jr., J. Non-Cryst. Solids 32, 313 (1979).

[22] Thermally induced H-D exchange was affected by heating the samples in a D_2 atmosphere at 200 psi and 800 °C for 24 h. This treatment generally followed a method described by J. Vitko, Jr. [J. Appl. Phys. 49, 5530 (1978).]

[23] Samples of α quartz enriched in ^{17}O were grown by E. Kostiner at the University of Connecticut, using a nutrient of SiO_2 powder enriched to 43 at.% ^{17}O and an aqueous phase ~0.5 M in NaOH and containing 30% ^{17}O by weight.

[24] For a review, see, D. L. Griscom, in *The Physics of SiO_2 and its Interfaces*, edited by S. T. Pantelides (Pergamon, New York, 1978), p. 232.

[25] K. L. Brower, Phys. Rev. B 20, 1799 (1979).

[26] Al-doped silica samples were provided by G. H. Sigel, Jr. [See, G. H. Sigel, Jr., J. Non-Cryst. Solids 13, 373 (1973/74).]

[27] P. C. Taylor and P. J. Bray, J. Magn. Reson. 2, 305 (1970).

[28] Also used as a constraint in this simulation were the g-value distributions determined in Ref. 14 for the E' center in glassy silica. For simplicity, the following approximations and assumptions were made: First, in the one-^{17}O case, it was assumed that the hf coupling constants were linearly correlated with the g shifts. This assumption had little practical effect on the outcome, however, since the distribution of hf coupling constants turned out to be broad with respect to the widths of the g value distribu-

tions. Second, the two-^{17}O case was approximated by a system with a fictitious nuclear spin of five and a discrete g matrix characteristic of α quartz. The eleven hf lines were properly weighted, 1:2:3:4:5:6:5:4:3:2:1. Finally, the three-^{17}O case, accounting for only 4.7% of the overall intensity, was neglected (as were any quasiforbidden transitions which might contribute to the spectrum).

[29] The small magnitude of the measured ^{17}O hfs splittings also comprises independent disproof of the E'-center model of Ref. 13.

[30] A. M. Portis, Phys. Rev. 100, 1219 (1955); J. S. Hyde, *ibid.* 119, 1483 (1960).

[31] C. S. Brown and L. A. Thomas, J. Phys. Chem. Solids 13, 337 (1960).

[32] Because of the strongly overlapping wings of the intense central resonance it is not possible to deconvolute the close-in portions of the 12.6-G hfs nor to determine accurately the relative intensity of this structure. Nevertheless, computer simulations can establish reliable upper limits on the magnitudes of hf coupling constants by fitting the outer reaches of these satellite lines.

[33] An independent estimate of the efficiency of the H-D exchange process is provided by the conversion of a proton-associated 74-G hf doublet to a triplet structure having a 22.7-G overall splitting (cf., J. Vitko, Jr., Ref. 22). In the present experiment, a vestigial 74-G doublet indicated that the exchange was incomplete.

[34] J. A. Weil and J. H. Anderson, J. Chem. Phys. 35, 1410 (1961).

[35] The intensity of the 12.6-G hfs relative to the central line is estimated range between 3 and 10% for the samples of Fig. 6. (See Ref. 32, however.)

[36] The spectra of Fig. 8—unlike all other spectra displayed in the present work—were obtained for a sample which had been heated to 1000 °C in flowing H_2 prior to γ irradiation. As discussed in Ref. 14, this process creates additional oxygen vacancies, thereby increasing the yield of E' centers. Considerable care was taken to ascertain that the spectra of this H_2 treated sample were identical (except for a significant improvement in signal-to-noise ratio) with the spectra of the same (and, one other) ^{29}Si-enriched sample when annealed in air prior to irradiation.

[37] H. Seidel and H. C. Wolf, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 557.

[38] For convenience in visual comparison, the simulations of Fig. 9 assume that $g_1(\text{bulk}) = g_{\parallel}(\text{surface})$. Based on the dotted simulation (using the g value scale given in Ref. 11), $g_{\parallel}(\text{surface}) = 2.001\,75 \pm 0.000\,05$. This compares with $g_1 = 2.001\,76 \pm 0.000\,20$ for the E_1' center in α quartz (Ref. 2). It should be noted, however, that Hochstrasser and Antonini (Ref. 11) carried out comparison experiments which indicated that the E_1' g matrix for α quartz is characterized by principal values 0.000 2 larger than those reported in Ref. 2. Using a double-cavity arrangement, it was determined in the present experiment that $g_1 = 2.001\,68 \pm 0.000\,06$ for the E' center in glassy silica—subject to the assumption that $g = 2.002\,80$ for the Varian pitch standard sample. Values of g_2 and g_3 *relative* to g_1 can generally be measured to an accuracy of ±0.000 05 (Ref. 2). The distribution functions for g_2 and g_3 shown in Fig. 9(b) are the optimized result of 14 trial simulations, each approximated by 7–10 points in g-value space with a resolution of 0.0001 (Ref. 14).

[39] For a review of radiation effects in glasses, see, E. J. Friebele and D. L. Griscom, in *Treatise on Materials Science and Technology*, edited by M. Tomozawa and R. Doremus (Academic, New York, 1979), Vol. 17, p. 257, Glass II.