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E' center in glassy SiO_2: Microwave saturation properties and confirmation of the primary ^{29}Si hyperfine structure

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Electron-spin-resonance studies of a series of air-annealed samples of glassy SiO_2 having various degrees of enrichment (or depletion) in the ^{29}Si isotope have confirmed that a γ-ray-induced doublet of 420-G splitting is the ^{29}Si hyperfine structure of the well-known E' center. This finding validates the widely accepted model of the E' center as an unpaired electron spin in a dangling sp^3 hybrid orbital of a silicon bonded to three oxygens in the glass structure and eliminates a recently proposed alternative model. Continuous-wave microwave saturation measurements at ~9.2 GHz were carried out in order to establish spin-lattice relaxation behavior and to determine absolute line intensities in the low-power limit. The spin-lattice relaxation process for the ^{29}Si E' center is shown to be dominated by a hyperfine mechanism. Spin-lattice relaxation times T_1 could be extracted from the cw saturation data only by means of a semiempirical formulation differing from the usual approaches found in the literature.

I. INTRODUCTION

The E' center[1] is the best known radiation-induced paramagnetic defect center in both the glassy and α-quartz forms of silicon dioxide. Electron-spin-resonance (ESR) studies of the crystal[1,2] and the glass,[1,3] coupled with careful theoretical considerations[4] of the data, have led to a general model for this defect of an unpaired electron spin occupying a dangling sp^3 hybrid orbital of a silicon bonded to only three oxygens in the glass or crystal structure.[5] The cornerstone of this interpretation has been the observation of a pair of hyperfine lines having mean splittings of ~410[2] and 420[3] G in the crystal and glass, respectively. If it is assumed that this doublet is the ^{29}Si ($I=\frac{1}{2}$) hyperfine structure (hfs) of the E' center, the magnitude of the splitting establishes that the unpaired spin is in an orbital having ~24% Si-3s character.[2] The combined intensity of the two members of the 410-G doublet in α quartz was found to be ~5% of the intensity of the strong (central) E'-center resonance[2], in agreement with prediction based on the natural isotopic abundance of ^{29}Si (4.70%). In glassy silica, the 420-G doublet was reported[3] to have an intensity relative to the central line ~2.5 times larger than predicted for samples of two different ^{29}Si contents. This observation was tentatively attributed to "an isotope-dependent relaxation mechanism which renders the ^{29}Si sites less saturable than their ^{28}Si counterparts at the level of microwave power employed (~0.1 mW)".[3] On the other hand, similar disparities in the observed intensities of the 420-G doublet, together with an apparent correlation with hydrogen pretreatment, have led to the recent counter suggestion[6] that this doublet is due to proton, rather than ^{29}Si, hfs, and that the prevailing model for the E' center[2-5] is incorrect. The present work was undertaken with the principal aim of establishing once and for all the origin of the 420-G doublet and the correct model for the E' center. Pursuant to this goal, the cw microwave saturation properties of the E' center have been studied and room-temperature spin-lattice relaxation times have been estimated for this defect in silica glasses containing several different abundances of ^{29}Si.

A. Case for associating the 420-G doublet with protons

Shendrik and Yudin[6] have remarked on the wide variety of hydrogen-associated defects already characterized[7-9] in irradiated fused silicas by ESR. In particular, atomic hydrogen with a doublet splitting of 510 G has been observed following irradiation at cryogenic temperatures,[7] and two other doublets with splittings ~74 and 120 G have been shown to be associated with protons by deuterium substitution experiments.[8,9] Thus, apart from potential physical counter arguments, the existence of a proton-associated doublet with a 420-G splitting might seem plausible. As alluded above, the fact that the observed intensity of the 420-G doublet[10] is often far greater with respect to the central, E' line than predicted by the known abundance of ^{29}Si can be adduced to indicate that this particular doublet may not be ^{29}Si hfs of the E' center. Moreover, the ability to observe the 420-G doublet in electrically melted natural and synthetic silicas is greatly enhanced by heat treatment in hydrogen prior to irradiation.[6] Indeed, Griscom *et al.*[3] in their study of the 420-G doublet in

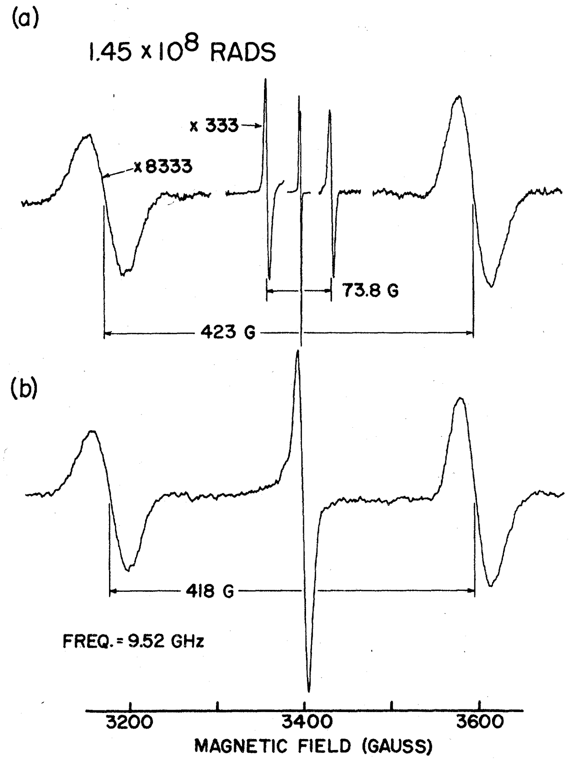

FIG. 1. X-band ESR spectra of amorphous SiO_2 samples γ irradiated and observed at room temperature. (a) Corning 7943, a low-OH silica which is fired in H_2 in the final stage of manufacture (Ref. 11). (b) 95% ^{29}Si-enriched silica treated in flowing H_2 at 1000 °C prior to irradiation. The 73.8-G doublet is due to a defect involving a proton. (After Ref. 3.)

glassy silica employed Corning 7943, an H_2-fired commerical silica,[11] and a ^{29}Si-enriched sample which had been treated at 1000 °C in flowing hydrogen (see spectra in Fig. 1). Finally, Shendrik and Yudin[6] reported that similar heat treatments in deuterium did not promote the observation of the 420-G doublet, although no corresponding triplet structure, predicted by the proton model, was observed.

B. Previous case for attributing the 420-G doublet to ^{29}Si hfs of the E' center

Griscom, Friebele, and Sigel[3] demonstrated that for silica glass samples containing either 5% or 95% ^{29}Si and studied at a common microwave power ~0.1 mW the following empirical relation obtains:

$$\frac{I(\text{central line})/N(^{28}\text{Si}+^{30}\text{Si})}{I(\text{420-G doublet})/N(^{29}\text{Si})}=\text{const}\,, \qquad (1)$$

where I is the ESR intensity determined by double numerical integration of spectra such as those of Fig. 1 and division by the spectrometer gain and N is the isotopic abundance. Although the measured value of the constant[3] (~0.4) on the right-hand side of Eq. (1) differed from its theoretical value of 1, the consistency of the result for two widely different ^{29}Si enrichments strongly suggested that the 420-G doublet must be ^{29}Si hfs associated with the central (E' center) resonance. The explanation offered for the discrepancy (see above) was not implausible; cases are known where the hyperfine interaction does exert a strong influence on spin-lattice relaxation[12,13] and hence differences in microwave saturation behavior might well be expected between E' centers with and without a magnetic isotope of silicon.

Since an influence of ^{29}Si on the relative intensities of the central line and the 420-G doublet structure is implied by Eq. (1), the fact that the samples of Ref. 3 were preheated in hydrogen was presumed to be irrelevant. The hydrogen treatment of the ^{29}Si-enriched sample was motivated by a study[14] which showed that the radiation yield of E' centers (and hence the signal-to-noise ratio for this particular defect) can be enhanced in this manner by a factor of 5–15, depending on the original method of sample manufacture. This consequence was understandable because hydrogen treatment of silica was expected to create additional oxygen vacancies,[14] and there is general agreement that the E' center is an oxygen-vacancy defect.[1–6]

C. Plan for a new experiment

In light of the latitude for disagreement implicit in the preceeding discussion, a plan was evolved for a new experiment. The principle features of this plan were (i) to obtain a wider range of silica samples both with respect to the degree of isotopic enrichment and the original method of manufacture, (ii) to subject these samples to common chemical and thermal treatments prior to irradiation, excluding if possible any pretreatment in hydrogen, (iii) to examine the microwave saturation behavior of both the central E'-center line and the 420-G doublet in order to determine whether or not the constant on the right-hand side of Eq. (1) has a dependence on microwave power level as previously suggested,[3] and (iv) to find out if this constant approaches unity at sufficiently low-microwave power levels.

II. EXPERIMENTAL

A. Samples

Isotopically enriched silicon dioxide was obtained from Oak Ridge National Laboratory (ORNL). One lot was enriched to 99.8% ^{28}Si and two other lots were enriched to 95.3% ^{29}Si. These materials are produced[15] by collecting the silicon isotopes in high-purity graphite which is then burned. The resulting ash is next fused in Na_2CO_3, dissolved in distilled water, filtered, and precipitated with perchloric acid. The precipitate is heated to drive off the remaining perchloric acid, washed, and ignited at 800 °C in platinum crucibles. Thus, the physical form of the enriched samples as delivered is a fine powder precipitate which is amorphous, but not vitreous. As noted previously,[3,14] far fewer paramagnetic defects can be induced in such precipitated materials than can be generated in *fused* silica by the same γ-ray dose. Accordingly, samples of the ORNL materials, including a 50-50 blend of the ^{28}Si- and ^{29}Si-enriched materials, were first sintered at 1100 °C to weld the fine particles together and then fused by brief exposures to a hydrogen-oxygen flame.

For comparison, one sample of silica containing silicon isotopes in their natural abundance was prepared by reacting distilled water with an excess of distilled $SiCl_4$ and evaporating to dryness. The resulting precipitate was then vitrified in the same manner as described above for the isotopically enriched samples. The final comparison sample was a coarsely ground specimen of Suprasil 1, a commerical fused silica produced by flame hydrolysis of $SiCl_4$.

The various glass samples described above were possibly characterized by different fictive temperatures, different hydroxol contents, and conceivably small differences in stoichiometry as initially prepared. To remove such random variables from the experiments which were to be performed, all samples were subjected to one final anneal in air, side by side in a furance at 1000 °C for 93 hours. Data provided by Vitko[16] indicate that this procedure should have caused the Suprasil 1 sample to outgas more than 70% of the OH groups initially present.

B. Irradiation and ESR spectrometry

One of the two ^{29}Si-enriched samples had been previously heated in hydrogen and irradiated by ^{60}Co γ rays to a dose of 9×10^7 rad (Si).[3] The microwave power saturation characteristics of the induced ESR spectrum [Fig. 1(b)] of this same sample were first investigated before subjecting it to the heat treatments described in the preceding paragraph. (It is reasonably expected that the 1000 °C anneal then removed all memory of the earlier irradiation.) This sample, together with the others which had not been previously irradiated, were weighed and sealed in evacuated fused silica tubes and subjected to further ^{60}Co γ irradiation. Radiation-induced defects in the tubes themselves were annealed out by heating one end to incandescence in a hydrogen-oxygen flame while the samples resided at the other (cool) end. An initial dose of 6×10^7 rad (Si) did not result in a satisfactory ESR signal-to-noise ratio for these air-annealed samples, so a cumulative dose of 3.2×10^8 rad (Si) was finally administered.

The ESR measurements described in this paper were all performed on a Varian E-9 spectrometer operating near 9.2 GHz. Except where explicitly noted, the data were obtained at room temperature, the laboratory magnetic field was modulated at 100 kHz, and the spectra were displayed as the first derivative of microwave absorption. Some studies were also carried out in the dispersion mode, as will be described in Sec. IV F. Absolute spin concentration measurements were accomplished by double numerical integration of the absorption spectra and comparison to the Varian strong pitch standard; the accuracy of this measurement is discussed in Sec. IV D. For this purpose, the central E' center resonance was obtained at modulation and power levels of 0.2 G and 0.2 μW, respectively, with a signal-to-noise ratio of 20 for the 69-mg sample of Suprasil 1. The 420-G doublet was measured at modulation and power levels of 20 G and 50 μW, with a signal-to-noise ratio of 10 for the 40-mg sample of ^{29}Si-enriched silica. In each instance the measured intensity was divided by the sample mass, and in the case of the 420-G doublet this specific intensity was multiplied by a factor of 1.4 to compensate for microwave saturation (see Sec. IV A).

III. THEORY

A. Microwave saturation

For typical ESR spectrometer systems involving a linear detector, the absorption signal is proportional to $\chi'' H_1$, where χ'' is the imaginary part of the complex susceptibility and H_1 is the amplitude of the rotating component of the microwave magnetic field.[17] The dispersion signal is proportional to $\chi' H_1$, where χ' is the real part of the susceptibility. For $H_1 \rightarrow 0$, χ'' and χ' are independent of H_1, so that the detected signals are simply proportional to H_1. However, at sufficiently high values of H_1, microwave saturation sets in and the values of χ' and/or χ'' diminish.

A quantitative theory of microwave saturation was worked out by Portis,[18] who considered the dependence of χ'' on H_1 for four different cases depending on the relative magnitude of the modulation frequency ω_m and whether the resonance line in question is homogeneously or inhomogeneously broadened.

A homogeneously broadened line is one that has a Lorentzian shape with a width determined by dipole-dipole interactions between like spins, spin-lattice relaxation, interaction with the rf radiation field, or exchange or motional effects.[17,18] If spin-spin interactions are dominant and the total number of like spins is <0.01 of the number of lattice sites, the rigorous theory of Kittel and Abrahams[19] gives the half-width as

$$\Delta H_L = 5.3 g \mu_B N \ , \tag{2}$$

where g is the g factor, μ_B is the Bohr magneton, and N is the volume concentration of unpaired spins. This half-width is formally related to the spin-spin relaxation time T_2 according to

$$T_2 = 1/\gamma \Delta H_L \ , \tag{3}$$

where γ is the magnetogyric ratio ($\approx 1.76 \times 10^7$ sec^{-1}/G).

Inhomogeneously broadened lines are commonly Gaussian in shape and are composed of a number (or continuum) of "spin packets" whose individual widths [e.g., Eq. (2)] are substantially less than the overall broadening. Sources of inhomogeneous broadening can be inhomogeneities in the dc laboratory magnetic field, unresolved hyperfine interactions with neighboring shells of magnetic nuclei, or statistical distributions in spin-Hamiltonian parameters such as are typically encountered in glasses.[20]

As will be seen in Sec. IV E, the product of the modulation frequency ω_m and the spin-lattice relaxation time T_1 is in all present cases greater than unity. Thus only two of the Portis relations need be considered, namely,[18]

$$\chi'' \propto 1/[1 + (H_1/H_{1/2})^2] \tag{4}$$

for homogeneously broadened lines and

$$\chi'' \propto 1/[1 + (H_1/H_{1/2})^2]^{1/2} \tag{5}$$

for inhomogeneously broadened lines, where $H_{1/2}$ is the value of H_1 at which the right-hand side of Eq. (4) becomes $\frac{1}{2}$ or the right-hand side of Eq. (5) becomes $1/\sqrt{2}$. The theoretical significance of $H_{1/2}$ has been debated, with Portis[21] having suggested a correction to his earlier interpretation[18] and Hyde[22] having argued for yet another conclusion. In summary, in the so-called Portis approach

$$H_{1/2} = 1/\gamma (T_1 T_2)^{1/2} \ , \tag{6}$$

provided $T_2 < T_1$ (Portis[21]) or $\gamma H_1 T_1 < 1$ (Hyde[22]). In what can be called the Hyde approach

$$H_{1/2} = 1/\gamma T_1 \ , \tag{7}$$

provided $T_2 > T_1$ (Portis[21]) or $\gamma H_1 T_1 > 1$ (Hyde[22]). In general, the conditions laid down by Portis and Hyde for the applicability of these two approaches can be conflicting. Thus, some kind of an experimental indication of the correct approach in any given case is desirable. It should be noted in passing that whereas the Portis original formulation[18] assumed amplitude modulation of the microwaves, his equations have been successfully employed in interpreting microwave saturation data obtained in the more standard field-modulation experiment (e.g., Ref. 23).

B. Measurement of H_1

For a microwave frequency of 9.5 GHz and a TE$_{102}$ cavity configuration, as employed in the present experiment, H_1 is given by[24]

$$H_1 = 1.41 \times 10^{-2} (Q P_0)^{1/2} \text{ G} \ , \tag{8}$$

where Q is the loaded quality factor of the cavity and P_0 is the incident power in watts. For present purposes, it was assumed that $Q = Q_0 \approx 7000$, where Q_0 is the unloaded Q.[25] Saturation data were obtained both with and without a fused silica Dewar insert. In this way it was empirically determined that the insert (which lowers the resonant frequency to 9.2 GHz) concentrates H_1 at the sample by a factor of 1.5. The value of P_0 was checked with a power meter, and errors in H_1 from all sources were estimated to be $\lesssim 10\%$.

IV. RESULTS AND DISCUSSION

A. Microwave saturation data

Typical microwave saturation results are plotted in Fig. 2 as A_{pp}/H_1, where A_{pp} is the peak-to-peak derivative amplitude of the ESR absorption signal. The amplitude, rather than the integrated intensity,

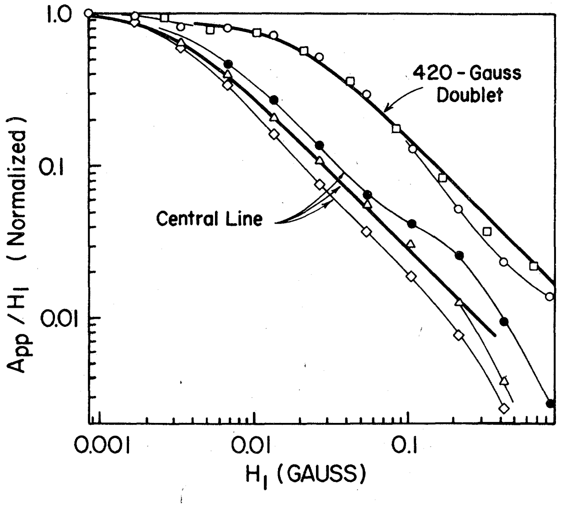

FIG. 2. Continuous-wave microwave saturation behavior at room temperature of the central, E' center resonance and the 420-G doublet in several fused silica samples following γ irradiation. Heavy curves are theoretical fits to the data described in the text. ● ○, ^{29}Si-enriched silica (H$_2$ annealed); □, ^{29}Si-enriched silica (air annealed); Δ, overlapping data points for samples containing 0 and 50% ^{29}Si (air annealed); ◇, Suprasil 1 (air annealed).

was used for this purpose as a matter of convenience, since the experimental line shape was found to be essentially invariant from the lowest microwave power levels to almost the highest (see below). These data were in turn divided by H_1 to facilitate comparison with the theoretical expressions of Eqs. (6) and (7) and the resulting numbers were normalized to unity at $H_1 = 0.000\,83$.

It can be seen clearly in Fig. 2 that the central (E') line saturates more rapidly than does the 420-G doublet. In particular, for the H_2-annealed sample at a power level of 0.1 mW ($H_1 \approx 0.018$ G), the normalized central-line intensity falls below that of the 420-G doublet by a factor ~0.3, which is identical with the constant factor of Eq. (1) previously determined for this same sample.[3]

It can be noted further that the saturation curve for the 420-G doublet is virtually independent of whether the sample had been preheated in H_2 (circles) or in air (squares). This result is in spite of the fact that the sample heated in hydrogen and irradiated to 9×10^7 rad was found to contain ~5 times more spins than the same sample subsequently annealed in air and reirradiated to 3.2×10^8 rad.

The saturation characteristics of the central E' center line exhibit definite sample-to-sample variation in Fig. 2. The possibility that any part of this variation might be an isotope-dependent effect is ruled out by the fact that the data points of the ORNL samples containing 0 and 50% ^{29}Si exactly overlap one another (triangles in Fig. 2), whereas the points for Suprasil 1 containing 5% ^{29}Si show a distinct tendency to saturate at lower values of H_1. The discrepancy between the ORNL samples and Suprasil is ascribed to cross relaxation to paramagnetic impurities in the former (the ORNL samples contain 200 ppm each of Fe and Cu according to the analysis supplied, whereas Suprasil 1 contains[26] 0.2 ppm Fe and 0.004 ppm Cu).

B. Evidence for inhomogeneous broadening

As discussed in Sec. III A above, the proper choice between Eqs. (4) and (5) to fit the saturation data depends on the nature of the line broadening. In the case of the 420-G doublet, the broadening has been shown by Griscom *et al.*[3] to be inhomogeneous. Specifically, the successful computer simulation of the experimental line shape was shown[3] to be dependent upon a statistical distribution, ~35 G in half-width and nearly Gaussian in shape, in the isotropic part of the hyperfine coupling constant which characterizes this doublet. Such statistical distributions in spin-Hamiltonian parameters over an ensemble of otherwise identical defects is common in glasses[20] and constitutes one of the possible modes of inhomogeneous broadening.

By contrast, the central E' line is quite narrow, having a peak-to-peak width ~2 G at 9 GHz. Whereas most of this width is known to be due to the anisotropy in the g tensor,[1] it will be the intrinsic "single-crystal" broadening which will determine the response of the resonance to microwave saturation. The first step in deconvoluting this intrinsic broadening from the powder pattern line shape involved determination of the modulation dependence of the spectrum. It was found that the shape of both Suprasil 1 and the ^{28}Si-enriched (0% ^{29}Si) sample became independent of modulation amplitude below ~0.3 G. With this fact established, a computer simulation[27] was carried out of the line shape in the low modulation limit. The results, shown in Fig. 3, indicate a distinct distribution in g values and a Gaussian single-crystal broadening function of half-width $\lesssim 0.18$ G. A similar study showed the central line of the 95% ^{29}Si-enriched samples to be characterized by essentially the same g tensor but a substantially broader Gaussian convolution function (half-width ~0.35 G). The latter broadening is almost certainly due to superhyperfine interactions with next-nearest-neighbor ^{29}Si nuclei, an inhomogeneous broadening

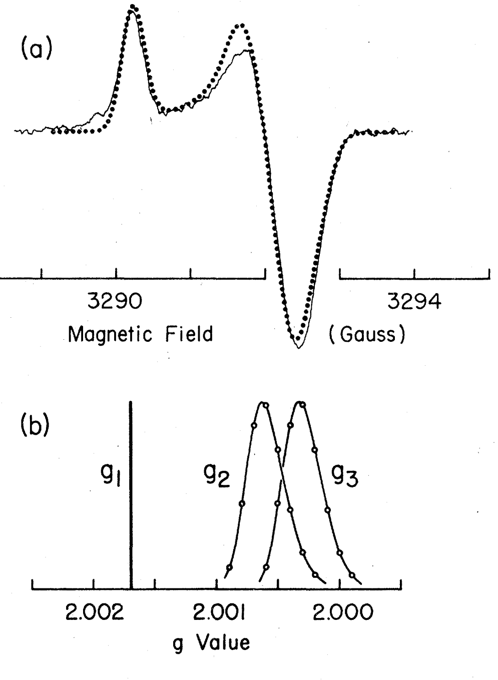

FIG. 3. X-band ESR spectrum of the E' center in glassy silica associated with nonmagnetic silicon isotopes. The experimental spectrum [unbroken curve in (a)] has been computer simulated (dotted curve) using the g-value distributions shown in (b). The shapes of the g_2 and g_3 distributions were derived under the assumption of a Gaussian distribution in energy splittings determining the g shifts (see Ref. 20); the mean g values are the same as those reported (Ref. 1) for the E_1' center in α quartz.

mechanism. Moreover, the g value distributions of Fig. 3 also constitute one mode of inhomogeneous broadening. The minimum broadening determined, of halfwidth 0.18 G, can be compared with the theoretical spin-packet width of ~0.007 G calculated from Eq. (2) using the measured spin concentration (Sec. IV D). On this basis, it was assumed that the Portis theory for *in*homogeneously broadened resonance lines [Eq. (5)] is appropriate to all of the present spectra.

C. Curve fitting

The experimental data of Fig. 2 have been fitted by Eq. (5) as indicated by the boldly drawn curves. Two adjustable parameters were used in these fits, namely, $H_{1/2}$ and a normalization factor. Whereas the best-fit normalization factor for the central line was 1.0, a value ~0.9 was required to fit the 420-G doublet. The latter fact is due to a small inflection in the experimental data of unknown origin near $H_1 \approx 0.003$ G.

For completeness, an attempt was also made to fit the data of Fig. 2 with the Portis expression for the saturation of a *homogeneously* broadened resonance line [Eq. (4)]. It was found that this relation did seem to give a better fit to some of the central-line data obtained for Suprasil 1 in a restricted set of H_1 values below ~0.005 G. However, Eq. (4) was clearly inappropriate to the data obtained over most of the range of microwave fields employed ($0.005 \lesssim H_1 \lesssim 0.1$ G), thereby providing confirmation of the conclusion reached in Sec. IV B that all lines are inhomogeneously broadened.

Above $H_1 \approx 0.1$ G, the central-line data of Fig. 2 are seen to deviate substantially from the form of Eq. (5) and in fact begin to follow the theory for homogeneously broadened lines [Eq. (4)]. The latter observation is simply understood, however, in terms of the effect of saturation on the Lorentzian spin-packet linewidth. Specifically, solution of the Bloch equations under slow passage conditions predicts[17]

$$\Delta H_L^{\mathrm{eff}}(H_1) = \Delta H_L(0)\,[1 + (H_1/H_{1/2})^2]^{1/2} \;, \qquad (9)$$

where $\Delta H_L(0)$ is given by Eq. (2). Indeed, for values of H_1 in excess of 0.1 G, a distinct broadening of the experimental central line (exceeding the inhomogeneous broadening determined in Sec. IV B) was observed and was accurately computer simulated using Eq. (9) to predict the width of the Lorentzian convolution function. The value of $H_{1/2}$ determined in this manner was in fact the same value determined by fitting the central-line data of Fig. 2 by Eq. (5) at lower values of H_1. This result is an added indication of the general validity of the Portis theory in interpreting the present cw microwave saturation data.

D. Spin concentrations

The absolute spin concentrations for the central E'-center line in the sample of Suprasil 1 which absorbed 3.2×10^8 rad (Si) was determined to be 3.3×10^{16} spins/gram (7.3×10^{16} spins/cm^3). The accuracy of this absolute measurement is subject to a number of possible errors, including a ±25% error in the calibration of the reference sample; an overall error ca. ±50% is presumed. On the other hand, the precision in comparing one sample to another (or in comparing the central line intensity to that of the 420-G doublet) can be better than ±10% where the signal-to-noise ratio is favorable.

Figure 4 displays the relative spin concentrations determined for both the central and doublet resonances for all of the samples of the present study following the outgassing treatment described in Sec. II A and subsequent ^{60}Co γ irradiation to a dose of 3.2×10^8 rad (Si). Here it can be seen that the 420-G doublet intensities in samples enriched to 95% in ^{29}Si are equal within the experimental scatter to the central-line intensity in samples containing $\lesssim 5\%$ ^{29}Si. It is emphasized that this equivalency was established by actual numerical integration of both spectra with a carefully determined correction for microwave saturation effects (Sec. II B). Moreover, all other data points, including those for the 50%-^{29}Si–50%-^{28}Si sample fall near the appropriate diagonal lines illus-

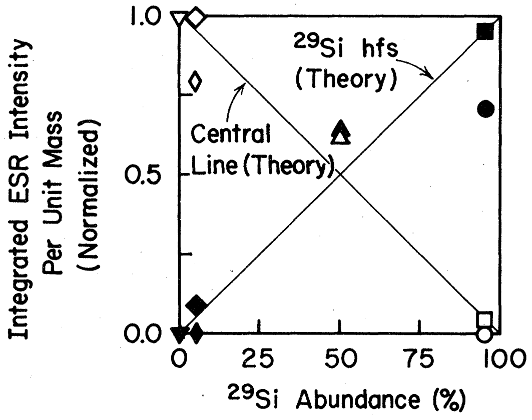

FIG. 4. Integrated ESR absorption intensities per unit sample mass for the E' center spectrum of Fig. 3 ("central line") and the 420-G doublet observed in air-annealed, γ-irradiated samples of fused silica containing various abundances of ^{29}Si. All data were normalized by dividing by the central-line intensity for the ^{29}Si-free sample. ◆◇, Suprasil 1; ♦◇, NRL precipitated silica; ▼▽, ^{28}Si-enriched silica (ORNL); ■□, ^{29}Si-enriched silica 1 (ORNL); ●○, ^{29}Si-enriched silica 2 (ORNL); ▲△, glass containing 50% ^{28}SiO$_2$ and 50% ^{29}SiO$_2$. Filled symbols pertain to the 420-G doublet, open symbols to the central line. Theoretical curves assume that the 420-G doublet is the primary ^{29}Si hfs of the E' center.

trating the theoretical behavior predicted under the assumption that the 420G doublet is in fact the primary ^{29}Si hyperfine structure associated with the central E' center resonance. This completes the proof that the constant on the right-hand side of Eq. (1) approaches unity as $H_1 \rightarrow 0$.

Taking into consideration a number of possible sources of error, part of the scatter in the overall resonance intensity of Fig. 4 (central line plus doublet) is tentatively ascribed to small sample-to-sample differences in glass structure which survived the preirradiation heat treatment and/or to impurity effects. It should be noted that some of the data points which are identically zero in Fig. 4 are related to poor signal-to-noise ratios encountered at the conservative levels of power and modulation which were employed for this measurement (Sec. II B). A central line was actually detected at higher power and modulation levels in both samples containing 95% ^{29}Si, and a 420-G doublet was detected in both samples containing 5% ^{29}Si, whereas the doublet was definitely absent from the sample containing 99.8% ^{28}Si (see Sec. IV F, below).

E. Relaxation times

Inserting the measured spin concentration of 7.3×10^{16} spins/cm^3 into Eqs. (2) and (3), one calculates a spin-spin relaxation time $T_2 = 7.9 \times 10^{-6}$ sec for the E' center in the air-annealed samples receiving a dose of 3.2×10^8 rad (Si). In the Portis approach, this number could be used in conjunction with Eq. (6) and the values of $H_{1/2}$ determined by curve-fitting (Sec. IV C) to calculate a value of T_1. In the Hyde approach, T_1 is calculated from Eq. (7) independent of the value of T_2. As discussed in Sec. III A, however, it first must be determined which approach, if either, is valid.

The basic phenomenology of the approaches due to Portis[18,21] and Hyde[22] are illustrated in Fig. 5 for the case of an inhomogeneously broadened resonance line where $T_2 < T_1$. The behaviors in regions I and III are not disputed, that is, for $H_1 << 1/\gamma T_1$ there is no saturation and for $H_1 >> 1/\gamma T_2$ the imaginary part of the susceptibility depends on H_1 as $1/\gamma H_1 T_1$. In the intermediate region II, Portis and Hyde predict different results; each assumes $\chi''(H_1)$ follows Eq. (5) but with Hyde believing $H_{1/2}$ to occur at $H_1 = 1/\gamma T_1$ (long dash) and Portis believing that $H_{1/2}$ is reached at $H_1 = 1/\gamma(T_1 T_2)^{1/2}$ (short dash). As indicated by the dotted curves, in the Portis approach there must be a deviation from the form of Eq. (5) between regions II and III. A deviation of this type is noted in Fig. 2 for the central E' line in Suprasil 1 but not in the ORNL silicas. However, the presence or absence of such small inflections is scant evidence for choosing between the two approaches. Indeed, if an inflection were to occur near $H_1 = 1/\gamma(T_1 T_2)^{1/2}$, an approach intermediate to those of Hyde and Portis would be clearly indicated. According to the validity criterion laid down by Portis,[21] the data should follow the Portis curve over most of region II whenever $T_2 < T_1$, while by contrast Hyde concludes that for $T_2 < T_1$ the data should approach the Hyde curve for H_1 values just above $1/\gamma T_1$. Both authors are in agreement that the Hyde curve would be followed in region II when $T_2 > T_1$, although it is not immediately clear why an inflection in the data should not still occur in this circumstance near the beginning of region II.

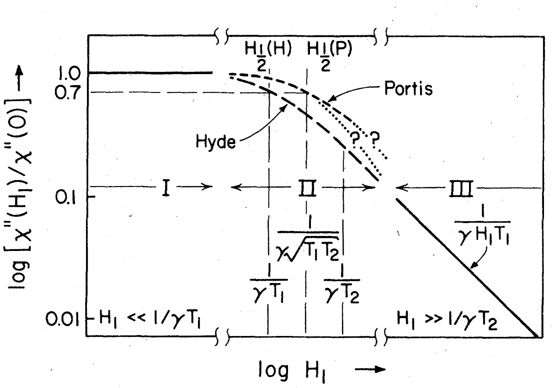

FIG. 5. Theoretical cw saturation behavior of an inhomogeneously broadened paramagnetic resonance line for the case $T_2 < T_1$. Contrasting predictions of Portis (Refs. 18 and 21) and Hyde (Ref. 22) are indicated.

With the object of resolving these issues in the case of the central E' line in silica, a study was carried out of the temperature dependence of the saturation curves for Suprasil 1. Specifically, full saturation curves were obtained at 20 °C temperature intervals between 100 and 300 K. These data were multiplied by the temperature at which they were acquired (in order to compensate for the difference in Boltzmann factors), divided by H_1, and plotted as a family of curves on the same graph. Thus, even though the low-temperature spectra were significantly saturated at the lowest power levels, it was possible to determine true $H_{1/2}$ values for all curves directly without the use of arbitrary fitting procedures. These values were used in Eq. (6) to determine the temperature dependence of $1/T_1$ in the Portis approach (circles in Fig. 6). Given the fact of inflections in the data near and above $H_1 = H_{1/2}$ (e.g., Fig. 2), $1/T_1$ in the Hyde approach [Eq. (7)] was also obtained by fitting the data between $H_1 \approx 0.01$ and 0.05 G by Eq. (5) (squares in Fig. 6). The latter procedure favors the Hyde approach because it ignores the first part of region II and may possibly probe region III as schematically indicated in Fig. 5.

The relative merits of the Portis and Hyde approaches in interpreting these data can be assessed by comparing the respectively calculated data points in Fig. 6 with the relaxation rate results of Castle and

Feldman[28] for the E_1' center in Corning 7943 fused silica (lower, boldly drawn curve in Fig. 6). The Castle and Feldman data were obtained by an inversion recovery method and were fitted by a small term linear in temperature plus two additional terms of the form

$$(1/T_1)_i = C_i[e^{x_i}/(e^{x_i}-1)^2] \ , \tag{10}$$

where C_i is a constant and $x_i = \hbar\omega_i/kT$. The lower curve in Fig. 6 is generated by taking $C_1 = 4.7$ sec^{-1}, $C_2 = 1900$ sec^{-1}, $x_1 T = 20$ K, and $x_2 T = 209$ K,[28,29] the linear term being negligible above ~10 K.

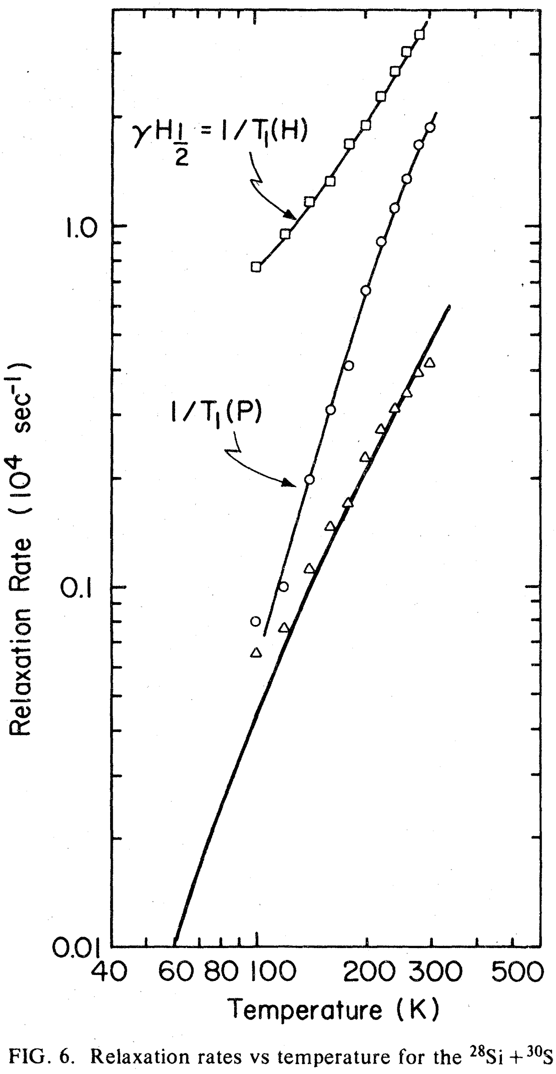

FIG. 6. Relaxation rates vs temperature for the ^{28}Si + ^{30}Si E_1' center in Suprasil 1 fused silica as derived from cw saturation in data the Hyde approach (squares) and the Portis approach (circles). The triangles represent the same data analyzed by a semiempirical approach described in the text. The lower, boldly drawn curve illustrates the temperature dependence of $1/T_1$ for the same defect in Corning 7943, as determined by an inversion-recovery technique (Ref. 28).

It is seen in Fig. 6 that $1/T_1(H)$ obtained from the cw saturation data in the Hyde approach depends on temperature approximately as $T^{1.5}$, whereas the results of Castle and Feldman follow an approximate T^2 behavior and lie roughly an order of magnitude lower. This striking disagreement is exacerbated if the true $H_{1/2}$ values are substituted for those obtained by curve fitting at higher values of H_1. Since the errors in determining $H_{1/2}$ by either method could scarcely be larger than ±15%, there is no way of reconciling the cw results in the Hyde approach with the relaxation rates determined by the inversion recovery method. By contrast, the cw data analyzed in the Portis approach nearly join the inversion recovery curve near $T = 100$ K. Thus, the Portis approach to the present analysis might be deemed appropriate if (i) the E' centers in Suprasil 1 and Corning 7943 can be shown to be equivalent and (ii) the discrepancy between $1/T_1(P)$ and the inversion recovery curve at higher temperatures can be explained.

Although Corning 7943 was not an original object of the present study, one sample was available which had been previously γ irradiated to a dose of 1×10^8 rad (Si). The cw saturation characteristics of this specimen were determined both before and after a 10-min anneal at 600 °C. This anneal was performed to reduce its spin population by a factor of 15 to a level commensurate with those of the air-annealed samples of this study. After the 600 °C anneal, $1/T_1(P)$ at room temperature for the E' center central line in Corning 7943 was found to be slightly *larger* than the value for the air-annealed Suprasil 1 sample containing approximately the same number of spins. Thus, the discrepancy in Fig. 6 between the present cw results and the inversion recovery data of Castle and Feldman is demonstrated to be related to the *methods*, rather than the samples employed.

The fast-sweep inversion-recovery method of Castle and Feldman[28] was described in more detail in an earlier paper.[30] In these measurements the E' center spin population was completely inverted and was observed to recover with a single time constant at each temperature; these time constants were found to be independent of spin density for spin concentrations varying by a factor of ~30. Since the entire E' center population was observed before and just after inversion, the possible existence of a sizeable subpopulation of centers with much shorter relaxation times is eliminated. Thus, the nonconformity of the present cw saturation results with the relaxation rate data of Castle and Feldman must be laid to deficiencies in the cw method. Moreover, a further test of the Portis approach is provided by the concentration independence of the T_1 values measured by Castle and Feldman. Indeed, for all of the samples of the present study which were investigated at different spin concentrations, $T_1(P)$ was found to vary widely. For example, reduction of the spin density in the sample of 7943 by a factor of 15 resulted in a decrease in $T_1(P)$ by nearly a factor of 7. It is finally apparent, therefore, that *neither* the Hyde nor the Portis approach is valid for deriving spin-lattice relaxation times from cw saturation data, at least not in the case of the E' center in fused silica.

Notwithstanding the failure of the Portis and Hyde approaches, it seems reasonable to assume that there exists a connection between the cw saturation data and the actual values of T_1. It is in fact possible to construct a semiempirical expression bringing the cw saturation data into agreement with the findings of Castle and Feldman. Obviously, the first step in this construction must be to force the calculated values of T_1 to be independent of spin concentration and hence independent of T_2. To do this, one first generalizes Eqs. (6) and (7) into the form

$$H_{1/2}=A^{1-x}/\gamma T_1^{1-x}T_2^x \quad , \tag{11}$$

where x may take on values between 0 (Hyde approach) and 0.5 (Portis approach) and A is an adjustable constant [equal to unity in Eqs. (6) and (7)]. T_2, as before, is calculated from Eqs. (2) and (3). The relevant value of x was determined in the present case by solving Eq. (11) for T_1,

$$T_1=A\,(\gamma H_{1/2})^{-1/(1-x)}\,T_2^{-x/(1-x)} \quad , \tag{12}$$

and equating the resulting expressions for Corning 7943 before and after reducing the spin concentration by a factor of 15. The number so derived, $x \approx 0.14$, also brought into approximate agreement the T_1 values calculated for the central line in the air-annealed and H_2-annealed isotopically enriched samples of Fig. 2, between which the spin concentrations varied by a factor of 5.

Good agreement between the present temperature-dependence data for Suprasil 1 and the relaxation rates measured by Castle and Feldman was achieved by means of Eq. (12) by using $x=0.14$ and taking $A=10$ (triangles in Fig. 6). The large discrepancy between the empirical and theoretical values of A is not presently understood, however.

Table I lists all of the room-temperature spin-lattice relaxation times estimated in the present study by means of Eq. (12), using $x=0.14$ and $A=10$. For comparison, values of T_1 are also listed for the $^{28}Si+^{30}Si$ E_1' and E_2' centers in α quartz and for the E_1' center in Corning 7943, as extrapolated to room temperature from the data of Castle *et al.*[31] and Castle and Feldman,[28,29] respectively. In α quartz, both the E_1' and E_2' centers have been attributed to unpaired spins in dangling sp^3 hybrid orbitals of silicons at the sites of single oxygen vacancies.[2,32] Apparently, the main differences between the E_1' and E_2' variations concern (i) on which side of the vacancy the spin is localized[32] and (ii) the fact that the E_2' center is associated with a proton [$A_{\parallel}(^1H)\approx 1.4$ G].[33] The first of these two distinctions is crystallographic in nature and cannot be made in a glass. Since the air-annealed samples of the present study were presumably well outgassed prior to irradiation (Sec. II A) and display central-line E' center spectra with no resolved hfs of the order of 1 G (Fig. 3), it is reasonably assumed that most of the E' centers in these glasses

TABLE I. Spin-lattice relaxation times at 300 K for E' centers in fused silica and α quartz.

Defect	Material	Spin Concentration (g^{-1})	T_1 (sec)	Method[a]
$^{28}Si+^{30}Si$ E_1' center:	Suprasil 1	3.3×10^{16}	2.9×10^{-4}	cw saturation[b]
	ORNL silica #2	3.3×10^{16}	2.4×10^{-4}	cw saturation[b]
	α quartz	2.0×10^{16}	2.3×10^{-4}	inversion recovery[c]
	Corning 7943	$\{1.5\times10^{18}$		
		4.5×10^{16}	2.1×10^{-4}	inversion recovery[c]
	ORNL silica #1	1.6×10^{17}	2.0×10^{-4}	cw saturation[b]
	Corning 7943	$\{3.3\times10^{16}$		
		5.1×10^{17}	2.0×10^{-4}	cw saturation[b]
$^{28}Si+^{30}Si$ E_2' center:	α quartz	1.0×10^{16}	1.4×10^{-4}	inversion recovery[c]
^{29}Si E_1' center:	ORNL silica #1	$\{3.3\times10^{16}$	2.3×10^{-5}	
		1.6×10^{17}	3.1×10^{-5}	cw saturation[b]

[a] Note that the inversion-recovery determinations of T_1 constitute absolute measurements, whereas the cw-saturation results are adjusted by means of an empirical scaling factor (see text).

[b] This work. Values calculated from Eq. (12), using $x=0.14$ and $A=10$.

[c] Extrapolated to room temperature from data obtained below 250 K by Castle and Feldman (Ref. 28) or Castle *et al.* (Ref. 31) using theoretical expressions and fitting parameters given by the respective authors (see Ref. 29, however).

are of the E_1' type. The defects in Corning 7943 were previously identified as E_1' centers on the basis of their optical spectra.[34]

One of the most striking results of Table I is the much shorter[35] value of T_1 which characterizes the ^{29}Si E_1' center (420-G doublet) vis-à-vis the ^{28}Si$+^{30}$Si E_1' center (central line). This result is here attributed to a hyperfine mechanism of spin-lattice relaxation, in analogy to previous conclusions regarding the F center in KCl,[12,13] and in confirmation of a suggestion made earlier.[3] That is, when the unpaired spin is trapped on a ^{29}Si site, the dominant coupling of the electron spin to the lattice is via the phonon-modulated dipole-dipole interaction between the electron and nuclear magnetic moments. To the author's knowledge, the present work constitutes the first example of a paramagnetic center with a hyperfine spin-lattice relaxation mechanism which has been verified by direct isotopic substitution.

F. Measurements in the dispersion mode

It has been known since the early work of Portis[18] that, for inhomogeneously broadened paramagnetic resonance lines, the dispersion signal χ' does not saturate at values of H_1 sufficient to severely saturate the absorption line χ''. For this reason, a series of dispersion mode spectra were obtained in an effort to increase the signal-to-noise ratio sufficiently to clearly identify the ^{29}Si hfs of the E' center in air-annealed glass samples containing ~5% ^{29}Si. The best-effort results of this enterprise are presented in Fig. 7, where all traces were obtained at a fixed power level of 12.5 mW and a constant (±10%) product of sample mass times spectrometer gain. The proportionality between the 420-G doublet dispersion mode signal and the fraction of ^{29}Si present is clearly evident, in agreement with the integrated areas under the absorption curves obtained at much lower power levels (Fig. 4).

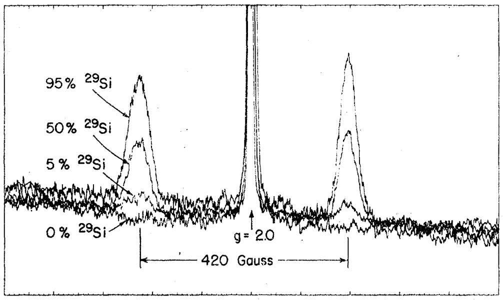

FIG. 7. Rapid passage dispersion mode ESR spectra at 9.2 GHz of a series of air-annealed, γ-irradiated fused silicas of diverse ^{29}Si contents.

G. Passage effects

The quantitative measurements of absorption intensity as a function of isotopic abundance ratio described above are valid only if some of the more difficult-to-quantify passage effects[36] sometimes encountered in paramagnetic resonance are avoided. All of the measurements reported in the present work were performed with 100 kHz field modulation because of the better signal-to-noise ratio generally afforded over lower modulation frequencies. However, it was verified that the basic central line shape illustrated in Fig. 3 is insensitive to lowering the modulation frequency to 1 kHz if the microwave power is maintained at a sufficiently low value ($\lesssim 0.2$ μW). At higher power levels (or lower modulation frequencies for this fixed power level) distortions in this line shape were encountered for very low modulation amplitudes ($\lesssim 0.1$ G). The nature of this distortion can be described as an admixture of undifferentiated absorption signal superimposed on the normal first derivative of absorption. This effect is presumed to be due to inadvertent cross talk between the absorption signal which is being measured and the rapid-passage dispersion signal (*vide infra*). In any event, the effect was essentially eliminated at a modulation frequency of 100 kHz by careful tuning of the cavity and raising the modulation amplitude to just below the threshold of overmodulation (~0.25 G). Thus the line shape of Fig. 3 is believed to be very nearly the "true" first derivative of the absorption curve, i.e., $d\chi''/dH$.

As originally discovered by Portis[37] and discussed at length by Hyde,[38] under certain conditions when the spectrometer is tuned to detect the first derivative of dispersion $d\chi'/dH$ of an inhomogeneously broadened resonance line, what is detected instead is the envelope of the undifferentiated absorption curve χ''. The detected signal at the modulation frequency may lag the modulation field by either 90° or 180° depending on the inter-relationships among H_1, H_m, ω_m, T_1, and the scan rate.[38] The experimental spectra of Fig. 7 indeed bear a closer resemblance to χ'' than they do to $d\chi'/dH$. The conditions under which these spectra were obtained in fact satisfied the general conditions laid down by Hyde[38] for the observation of such rapid passage effects and, in addition, the special relations $H_1/H_m < 1 < \omega_m T_1$, $T_1\, dH_0/dt < H_m$ were also satisfied, leading to the prediction of a 180° phase relationship with the modulation. The latter prediction was experimentally confirmed. Another interesting effect was also noted, namely that as the modulation level was raised above ~1 G the signal level began to decrease and eventually disappeared for $H_m \approx 20$ G. This is evidently because at such high modulation levels one of the conditions for adiabatic rapid passage ($\omega_m H_m < \gamma H_1^2$)[38] becomes violated. The inability to employ modulations greater than ~1 G accounts for the unspectacular signal-to-noise ratio in Fig. 7.

In summary, the passage conditions encountered in the course of the present experiment were carefully circumscribed and appear to be understandable in terms of current theory.

H. Other resonances

A number of different intrinsic and extrinsic defect types have been identified in irradiated fused silicas by ESR methods (for a review, see Ref. 39). While the present study was focused on the E' center, certain other resonances were observed in the course of the isotopic enrichment experiments described here. Defects attributed to holes trapped on nonbridging oxygens [the "wet" oxygen-hole center (OHC)][40] were observed at high levels of microwave power and modulation; the ^{29}Si-enriched samples revealed ^{29}Si hyperfine splittings ~13 G similar to the ^{29}Si hfs observed for nonbridging oxygen hole centers in binary alkali silicate glasses.[20] Also observed in the less-pure ORNL samples was an overlapping spectrum of the so-called "Al" hole center,[39] which exhibited ^{29}Si hfs ~10 G in the ^{29}Si-enriched samples. This is consistent with the accepted model for the Al center of a hole trapped on an oxygen bridging between a silicon and a substitutional aluminum in the glass network (see, e.g., Ref. 39). An apparent doublet structure of splitting ~12 G centered on the central E' line, originally reported by Shendrik and Yudin,[6] was also recorded, but only for the samples containing 0 or 5% ^{29}Si. The immediate conclusion is that this 12-G structure, representing an intensity ~0.05 of the E' center, cannot be ^{29}Si superhyperfine structure of the E' center, and therefore is probably proton hfs as previously suggested.[6] A pair of proton hfs[8,9] lines centered on $g = 2.0$ and split by 74 G was also observed, but in very low intensity (~0.0005 relative to the E' center). The observation of the 12- and 74-G doublets demonstrates that a small number of protons (~0.2 ppm) remain even in silica samples subjected to outgassing at 1000 °C. The 74-G doublet, like the 12-G structure, was not observed in samples containing 95% ^{29}Si, but the signal-to-noise ratio was too poor to conclude definitely that the 74-G doublet has associated with it an additional hyperfine splitting due to ^{29}Si as implied by the model of Vitko.[9]

Finally, it is remarked that none of the resonances described in this section contributed any measurable interference to the E' center spectra elucidated above, due either to their low overall intensities or to fortuitous differences in g values, linewidths, hyperfine splittings and/or microwave power saturation characteristics.

V. SUMMARY OF CONCLUSIONS

The present study has led to the following significant conclusions:

(i) The 420-G doublet observed in irradiated fused silicas[3] (and, by inference, the 410-G doublet observed in α quartz[2]) is the primary ^{29}Si hyperfine structure of the E' center and is not due the involvement of a proton as lately suggested.[6] This reconfirms the basic structural picture of the E' center as an unpaired spin in the dangling sp^3 hybrid orbital of a silicon bonded to only three oxygens.[2,4,5]

(ii) The 420-G doublet is less susceptibile to microwave saturation than is the central E'-center line involving ^{28}Si and ^{30}Si nuclei. Thus the relative ESR intensities of the doublet and central line are given by Eq. (1), where the constant factor on the right-hand side may vary from ~0.1 to 1.0, depending on microwave power, spin concentration, and sample purity.

(iii) As confirmed by isotopic substitution, the short T_1 value estimated for the ^{29}Si E' center is due to the hyperfine mechanism of spin-lattice relaxation. This may be the first instance of a hyperfine relaxation mechanism being confirmed by direct isotopic substitution.

(iv) The conventional approaches to extracting spin-lattice relaxation times from cw saturation data are shown to be invalid, at least in the case of the E'-center central line in fused silica. An alternative, semiempirical approach is shown to yield consistent results over wide ranges of spin concentrations and temperature.

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