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Radiation-induced defects in dense phases of crystalline and amorphous SiO_2

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We have studied electron-spin resonance in unirradiated and irradiated samples of naturally occurring stishovite. An unidentified central resonance ($g \sim 2.0030$) with weak hyperfine lines is observed with a density 6×10^{14} per gram in unirradiated samples. Irradiation induces two sets of hyperfine lines, one sharp (1 G peak to peak) and one broad (14 G peak to peak) with hyperfine parameters $A_\parallel = 590$ G, $A_\perp = 457$ G (sharp) and $A_\parallel = 525^{+0}_{-15}$ G, $A_\perp = 503^{+7.5}_{-0}$ G (broad). The latter set is consistent with E_1' centers in densified, amorphous SiO_2 with $\rho \gtrsim 3.2$ g cm^{-3} while we identify the former with E_1' defects in crystalline stishovite. The hyperfine parameters for the crystalline phase cannot be interpreted simply in terms of the usual *s-p* electron model.

Stishovite is an octahedrally coordinated phase (SiO_6) of SiO_2 which can be fabricated at high temperatures and pressures[1] in the laboratory and is found naturally occurring in meteor impact craters in the Earth's surface.[2] It is particularly interesting because the phase forms through a transformation of crystalline quartz during which a spiral contraction of adjoining SiO_4 tetrahedra occurs[3] followed by a rebonding and reorganization once the Si-second-nearest-neighbor-O distance becomes small enough.[4,5] The Si coordination thus changes from four to six. Little appears to be known experimentally about the electronic structure of the sixfold-coordinated material and where data exists, there seems to be some disagreement between theory and experiment. For example, effective charges assumed in order to fit x-ray photoelectron spectroscopy (XPS) data[6] indicate that, as compared to tetrahedrally coordinated phases, electron transfer from the Si site to the O is larger. Calculations[7] of the band structures of crystalline SiO_2 polymorphs, including stishovite, suggest the reverse is true, in fact, a net increase in the number of electrons at the Si site of 0.4 is anticipated for the SiO_2 structure. Measurements of the ^{29}Si chemical shift by nuclear magnetic resonance[8,9] reveal the shift for stishovite (with respect to ^{29}Si in tetramethylsilane) to be ~ 90 ppm more negative than in α-quartz. Calculations for SiF_4 and SiF_6 analogs to the SiO_4 and SiO_6 molecules together with ligand charge arguments[10,11] suggest the shift results from an increased diamagnetic component and reduced paramagnetic term. Unfortunately, direct quantification of this result in terms of charge transfer is not possible because the paramagnetic and diamagnetic terms cannot be directly expressed as multiples of the electron densities but involve the band gap, band structure, etc.

In the present work we have performed preliminary electron-spin-resonance studies on natural samples of powdered, nominal stishovite obtained from the Arizona meteor impact crater.[12] Samples were studied as obtained and after irradiation with 7.5 Mrad of ^{60}Co γ rays at a rate of 0.33 Mrad per h. Resonance studies were carried out at room temperature or 100 K using a Bruker ER200D *X*-band spectrometer with 100-kHz magnetic field modulation. Experimental results for the derivative absorption spectra in unirradiated and irradiated samples are shown in Figs. 1(a) and 1(b), respectively. Supplementary structure appears in the central line shape after irradiation but this cannot be readily extracted by simple subtraction of Fig. 1(a) from 1(b). By double numerical integration and comparison with a strong pitch standard

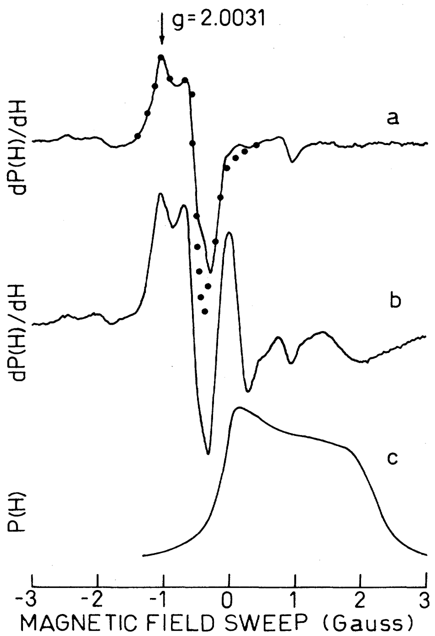

FIG. 1. Experimental electron-spin-resonance spectra (central resonance) in (a) unirradiated samples and (b) a sample irradiated with 7.5 Mrad ^{60}Co γ rays. The dots show the theoretical fit to the spectrum as described in the text. The power absorption spectrum in (c) is derived by subtracting the numerical integrals of (a) from (b). The central field taken as zero in the field sweep is 3361.6 G.

we estimate the paramagnetic spin density in the unirradiated sample to be 6×10^{14} g^{-1} (assumed spin $\frac{1}{2}$). Figure 2(a) shows the spectra observed in the irradiated sample in the magnetic field range 3000–3200 and 3500–3700 G. These lines are absent in the unirradiated sample spectra.

The magnetic field for resonance in the presence of a hyperfine interaction is given by[13]

$$H(m_I,\theta)=\frac{h\nu_0}{g\beta}+\left[\frac{K}{g\beta}\right]m_I-\frac{A_\perp^2}{4g\beta h\nu_0}\left[\frac{A_\parallel^2+K^2}{K^2}\right][I(I+1)-m_I^2]$$

$$-(2g\beta h\nu_0)^{-1}\left[\frac{A_\parallel^2-A_\perp^2}{K}\right]^2\left[\frac{g_\parallel g_\perp}{g^2}\right]^2\sin^2\theta\cos^2\theta\, m_I^2 \qquad (1)$$

with

$$g^2=g_\parallel^2\cos^2\theta+g_\perp^2\sin^2\theta\,,$$

$$K^2=(A_\parallel^2g_\parallel^2\cos^2\theta+A_\perp^2g_\perp^2\sin^2\theta)/g^2\,,$$

where θ is the angle between the applied magnetic field and the principal axis of the defect and/or impurity and ν_0 is the applied microwave frequency. We have assumed axial symmetry, otherwise $g_\perp=(g_1^2\sin^2\phi+g_2^2\cos^2\phi)^{1/2}$ with a similar expression for $A_\perp$ in terms of A_1 and A_2. $A_\perp^2g_\perp^2=A_1^2g_1^2\sin^2\phi+A_2^2g_2^2\cos^2\phi$. Since we have studied polycrystalline samples, an assumption of a particular absorption line shape (here chosen Lorentzian) and averaging over all θ (or θ and ϕ) was necessary to simulate the experimental spectra. In Fig. 1(a) the dots show the closest fit to the experiment attainable for which we deduce $g_3=2.0031$, $g_2=2.0028$, $g_1=2.0026$ with $\Delta H_L=0.11$ G (ΔH_L = Lorentzian absorption half width at half peak amplitude). The fit is not perfect and we observe evidence for a supplementary line corresponding to $g\sim2.0027$. Essentially equidistant on either side of the central structure we observe two lines (one split) which we attribute to a weak hyperfine structure with a splitting of 2.95 ± 0.15 G. Preliminary annealing studies at 270 °C suggest that these lines are correlated with the defect and/or impurity at the origin of the central spectrum. Since there are two peaks evident, we assume the nucleus producing this spectrum has a nuclear spin of $\frac{1}{2}$. It would appear that all of the centers contributing to the central spectrum do not "see" these nuclei. At the present time we believe that the whole central spectrum arises from impurities rather than from intrinsic structural defects.

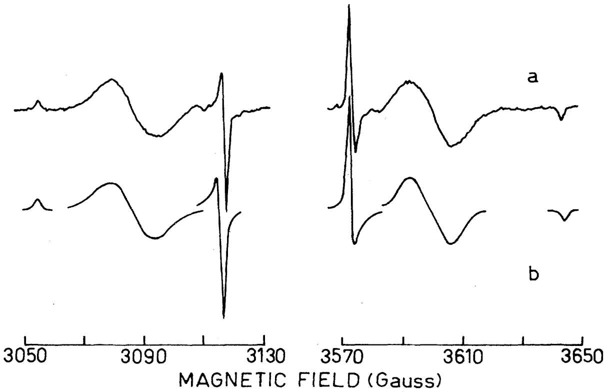

FIG. 2. Experimental derivative power absorption spectra in a sample irradiated with 7.5 Mrad of ^{60}Co γ rays (a) in the field sweep range 3050–3130 and 3570–3650 G. The sharp lines are identified with E_1' centers in crystalline stishovite and the broad lines with E_1' centers in densified, amorphous SiO$_2$. (b) The theoretical spectra determined as described in the text.

The spectra in Fig. 1(b) indicate that the central spectrum intensifies and new structure appears under irradiation. Furthermore, extra lines appear spaced approximately ±250 G on either side of the central spectrum [Fig. 2(a)]. By double numerical integration of the experimental central spectrum and associated 2.95-G hyperfine lines we estimate an increase of a factor of 2 in the population of defect centers giving rise to the "unirradiated" resonance spectrum for a γ dose of 7.5 Mrad. The proximity of the g factors for the unirradiated spectrum and the radiation-induced spectrum complicates deduction of the latter by simple subtraction. In Fig. 1(c) we thus show the difference in absorption line shapes obtained by the subtraction of the integrals of the experimental curves shown in Figs. 1(a) and 1(b). The resultant spectrum, supposedly due to radiation-induced centers, clearly contains two peaks at $g=2.0024$ and $g=2.0017$. The overall curve could not be simulated using Eq. (1) with any combination of g factors and/or linewidths. We will argue that the absorption curve in Fig. 1(c) results from the presence of at least two different defect centers.

The low-field and high-field resonance lines observed in irradiated samples shown in Fig. 2(a) were obtained using 500 times more gain than was used to record the central resonance spectrum of Fig. 1(b). This fact, coupled with the line shapes as compared with those observed in powdered α quartz[14] and in amorphous silica[15] after irradiation, lead us to conclude that these lines originate from oxygen vacancy center (E_1') defects involving the weakly abundant (4.7%) ^{29}Si nucleus. The sharp lines correspond to the crystalline phase, stishovite, and the broad lines, to a densified, amorphous phase. Without recourse to modeling for the sharp spectrum one can immediately deduce the values of $A_\parallel$ and $A_\perp$. We obtain $A_\parallel=590$ G and $A_\perp=457$ G, values significantly larger than those of α quartz, 455 and 392 G, respectively.[16,17] Using the $A_\parallel$ and $A_\perp$ values and approximating $g_\parallel=g_\perp=2.002$ we deduce the theoretical hyperfine spectrum shown in Fig. 2(b). The Lorentzian linewidth was 1 G. The broader peaks inside the sharp "crystalline" peaks are argued to be due to a densified amorphous SiO$_2$ phase coexisting with the stishovite. Since $A_\parallel$ and $A_\perp$ for them cannot be determined directly from experiment we have used Eq. (1) and a trial and error fitting procedure. Again assuming $g_{\parallel}=g_{\perp}=2.002$ [consistent with the deductions of Fig. 1(c)] we varied $A_{\parallel}$ and $A_{\perp}$. The symmetry of the hyperfine lines turns out to be a relatively sensitive function of $A_{\parallel}$ and $A_{\perp}$ and we are able to deduce limits of $A_{\parallel}=525^{+0}_{-15}$ G and $A_{\perp}=503^{+7.5}_{-0}$ G with $\Delta H_L=1$ G. To account for the width of the hyperfine lines it was necessary, as shown previously, to assume a Gaussian distribution of hyperfine parameters with probability: $p(A)=\exp\{-[(A-\bar{A})/\Delta A_G]^2\}$ with $\Delta A_G=14$ G. The theoretical spectrum is shown in Fig. 2(b). Finally, by double integration of the hyperfine spectra we were able to ascertain that the density of amorphous defects was approximately twice the density of crystalline defects.

In early work on E'_1 defects in α quartz it was argued that the s and p electron densities at the defect site could be estimated from the hyperfine parameters assuming[17] $a_s^2=A_{\text{iso}}/A_s$ and $a_p^2=A_{\text{anis}}/A_p$ where $A_{\text{iso}}=(A_{\parallel}+2A_{\perp})/3$, $A_{\text{anis}}=(A_{\parallel}-A_{\perp})/3$, and A_s and A_p were hyperfine coupling parameters assumed[18] to be 1473 G for A_s and 36 G for A_p. Our results for the amorphous phase suggest $a_s^2=0.346$ and $a_p^2\lesssim 0.21$. The sum $a_s^2+a_p^2=0.55$ is substantially smaller than the value of 0.85 deduced for α quartz and for undensified amorphous silica although a_s^2 is larger (0.35 as opposed to 0.24). Previous measurements[15] on densified silica demonstrate a continuous increase in A_{iso} with densification. From data obtained for samples having a densification ($d\rho/\rho$) up to 24% we can deduce a lower limit to the density of the present amorphous phase. With $dA_{\text{iso}}/A_{\text{iso}} \div d\rho/\rho \lesssim 0.0055$ per percent and assuming $A_{\text{iso}}=410$ G for undensified silica ($\rho=2.206\ \text{g cm}^{-3}$) we deduce $d\rho/\rho$ (amorphous to stishovite) $\gtrsim 44\%$. Consequently ρ (amorphous) $\gtrsim 3.3\ \text{g cm}^{-3}$. A similar analysis for the crystalline phase results immediately in a dilemma. From $A_{\text{iso}}=501$ G and $A_{\text{anis}}=44.3$ G (413 and 21 G in α quartz) we deduce $a_s^2=0.340$ and $a_p^2=1.23$. The value of a_s^2 is consistent with the amorphous result but a_p^2 is too large since clearly we expect $a_s^2+a_p^2\lesssim 1$. Since the density of stishovite is $4.29\ \text{g cm}^{-3}$, the large value of a_s^2 is not unexpected. A word of caution, however. If we perform the same analysis for α quartz we conclude that $\rho \sim 2.22\ \text{g cm}^{-3}$; substantially smaller than the experimental value of $2.6\ \text{g cm}^{-3}$ suggesting that the results obtained for the density and/or hyperfine constant relationship found for densified, amorphous silica may not be simply extrapolated to the crystalline phases.

In summary, our electron-spin-resonance measurements on powdered, natural stishovite reveal a strong, presently unidentified resonance near $g=2.0030$ with a spin density $6\times10^{14}\ \text{g}^{-1}$. Under irradiation this signal grows and we observe new irradiation-induced resonance lines which we identify as due to oxygen vacancy (E'_1) centers. The observed hyperfine spectra are used as evidence for the presence of both a highly densified amorphous phase and a crystalline phase (stishovite) in the samples. Such highly densified amorphous phases ($\rho \gtrsim 3.2\ \text{g cm}^{-3}$) have not been previously studied by resonance methods. The simultaneous presence of both a compact crystalline phase and a densified amorphous phase in natural samples is consistent with a model in which some α quartz undergoes a phase transformation under pressure to the sixfold coordinated stishovite form while some α quartz is shock amorphized.[19] The hyperfine splitting for the crystalline phase cannot be explained in terms of the standard s-p electron model and this may evidence the presence of other unaccounted for orbital character[20] (e.g., $3d$) or supplementary hyperfine interactions at the site of the localized electron. This point requires further investigation.

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