Paramagnetic Point Defect in Fluorine-Doped Silica Glass: The $E'(\mathrm{F})$ Center

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Fluorine-doped silica is a key material used in all low-loss and/or radiation-resistant optical fibers. Surprisingly, no fluorine-related radiation-induced point defects have been identified. By using electron paramagnetic resonance, we report the first observation of F-related defects in silica. Their fingerprint is a doublet with 10.5 mT splitting due to hyperfine coupling (hfc) to ^{19}F nuclear spins. An additional 44.4 mT hfc to the ^{29}Si nucleus indicates that this defect belongs to the "E' center" family and has a structure of a fluorine-modified Si dangling bond: 3-coordinated Si atoms with an unpaired electron in an sp^3 orbital, bonded to a glass network by 2 bridging oxygen atoms and to a F atom.

Introduction.—High-purity fluorine-doped synthetic silica is a material of utmost importance for low-loss optical telecom fibers, optical elements, and fibers used in radiation environments, with high-power lasers, or in the deep-ultraviolet (UV) spectral range. Fluorine doping in concentrations ~ 0.01 to ~ 5 wt.% is used in all depressed-index optical fibers to decrease the refraction index of the cladding and to reduce the Rayleigh scattering in ultra-low-loss fiber cores [1,2]; to increase the optical band gap and deep-UV transparency [3]; and to reduce the formation of color centers induced by ionizing radiation or by high-power lasers [4,5]. The beneficial effects of F doping are attributed to disruption of the continuous SiO_2 glass network by strong Si—F bonds, which allow it to relax and to reduce the number of strained Si—O bonds serving as defect precursors [6]. Due to the strength of the Si—F bond, and in a unique difference to any other dopant of SiO_2, fluorine does not introduce electronic states into the band gap of silica and even increases the effective optical band gap. Moderately F-doped silica is considered as the most radiation-resistant among all optical glasses.

Given the importance of F-doped silica and numerous dedicated studies, it is surprising that only the *intrinsic* radiation-induced defects, commonly occurring in pure, nondoped silica have been reported in it; no specific F-related defects have been detected [7]. Electron paramagnetic resonance (EPR) has served as the primary technique to determine the structures of the most important intrinsic defects in silica, Si-dangling bonds ($\equiv$Si°, E' centers) [8], oxygen dangling bonds ($\equiv$Si—O°, commonly denoted as NBOHC, nonbridging oxygen hole centers), and peroxy radicals ($\equiv$Si—O—O°) [9]. The key evidence on them was provided by analysis on hyperfine couplings (hfc) to magnetic nuclei ^{29}Si (4.7% abundance) and

^{17}O (in isotopically enriched samples). In this light, the absence of fluorine-related paramagnetic centers is particularly puzzling, since fluorine has nuclear spin I = 1/2 with 100% abundance and its hfc should give rise to easily detectable doublet lines in EPR spectra. The generally accepted tentative explanation states that the continuous SiO_2 glass network becomes well-relaxed when interrupted by Si—F formation, has no strained Si—O bonds as defect precursors, and therefore dangling-bond defects do not form close to fluorine sites. Because of the lack of experimental evidence there are no quantum chemistry calculations of F-related defects in silica.

In this Letter, we report the first observation of fluorine-related defects in silica glass, by using heavily F-doped samples irradiated by 2.5 MeV electrons, and EPR techniques optimized for detecting low-intensity and spectrally wide signals. The observed hfc with ^{19}F and ^{29}Si nuclei allows us to assign them to a fluorine-modified variant of Si dangling bond, termed here as the "$E'(\mathrm{F})$" center.

Experiment.—Five high-purity synthetic silica samples, fluorine-doped in range 0.5 to 7 wt% F were studied. To elucidate the effect of fluorine, seven additional, nondoped synthetic silica samples of different origins, stoichiometries, and silanol contents were measured in parallel. The samples were irradiated by 2.5 MeV electrons in a linear accelerator at room temperature in dose range 1.4–4.6 GGy or by 30 kV x rays with dose ~ 30 kGy. One control sample was irradiated by fast neutrons, dose 2.2×10^{18} n/cm^2. The sample properties are described in the Supplemental Material [10], Table S1. The fluorine content was checked by the relative intensity of the 935 cm^{-1} Raman band of Si—F vibrations (Fig. S1 [10]).

Optical absorption and photoluminescence (PL) spectra were measured by Agilent Cary 7000 and Edinburgh

FLS1000 spectrometers. EPR spectra were recorded using the Bruker Elexsys-II E500 X-band CW spectrometer. The "high-power 2nd harmonic out-of-phase" measurement mode was basically employed. It is based on an oscillating partial saturation of microwave absorption, which occurs twice per one magnetic field modulation cycle with $-\pi/2$ phase shift, due to the difference of dwell times at the middle and extremal field values within the field modulation width. With optimized microwave power and field modulation width it can yield a direct, nondifferentiated shape of the EPR absorption signal, and can significantly boost the sensitivity for wide signals, which are virtually invisible by the common derivative-mode technique. Starting from Ref. [11], it has been frequently used to detect ^{29}Si hfc of E' centers. The EPR spectra were analyzed using the EasySpin toolbox [12]. All measurements were performed at room temperature.

Results.—Figure 1 shows the EPR spectra of all F-doped (spectra A–E) and undoped (spectra F–L) samples, measured in high-power 2nd harmonics mode. The shape and intensity of the spectra were dependent on microwave power and modulation amplitude ΔH; the optimized
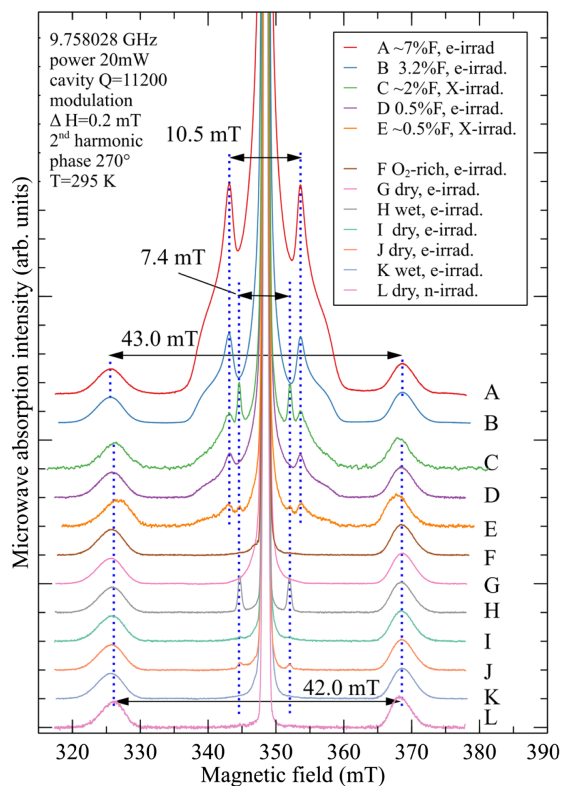

FIG. 1. High-power 2nd harmonic out-of-phase EPR spectra of irradiated fluorine-doped samples (spectra A–E) and fluorine-free samples (F–L). The indicated doublets with splittings 42–43, 7.4, and 10.5 mT are due to hyperfine coupling to ^{29}Si, ^{1}H, and ^{19}F (spin $I = 1/2$) nuclei. All spectra are independently normalized to have the same intensity of the ^{29}Si doublet high-field component at ~368 mT.

parameters are shown in Fig. 1. For the sample "A" with the highest F concentration the intensity of the signal was high enough to measure the same sample in the conventional, less-sensitive derivative mode, using 2×10^4 times lower microwave power (1 μW). Its shape (Fig. S4 [10]) was very close to the numeric derivative of the spectrum "A" in Fig. 1, thus confirming that Fig. 1 correctly represents the shapes of microwave absorption spectra.

The central peak (off scale in Fig. 1) corresponds to g-factor values ~2.0003, reminiscent of the E' centers [8,11], ubiquitous in irradiated silica. g values were determined more accurately using the low-power (400 nW) derivative mode. Very close g-tensor values were obtained (Fig. S3 [10]) both for F-doped sample "A" ($g_1 = 2.00026$, $g_2 = 2.00065$, $g_3 = 2.00175$) and pure sample "L" ($g_1 = 2.00036$, $g_2 = 2.00045$, $g_3 = 2.00177$).

All spectra in Fig. 1 show doublets with splitting ~42 mT, which increases to 43 mT in the strongly F-doped samples "A" and "B". A doublet with splitting 7.4 mT is present in the spectra of some doped (C, E) and undoped (H, I, J) samples. All F-doped samples (A–E) show a 10.5 mT doublet, with the largest intensity in the strongest-doped samples "A" and "B".

Photoluminescence spectra (see Fig. S2 [10]) did not reveal any significant differences between the strongly F-doped sample "A" and undoped samples. In both cases the usual radiation-induced 280 and 470 nm emission bands due to divalent Si (silicon oxygen deficiency centers [7,13]) and the 650 nm band of oxygen dangling bonds NBOHCs [7,14] were observed.

Discussion.—The 42 mT doublet, present in all spectra of Fig. 1, is a signature of E' centers [8,11], caused by hfc of unpaired electrons in Si sp^3- like dangling orbitals to ^{29}Si nucleus ($I = 1/2$, natural abundance 4.7%). The shift to 43 mT in strongly doped samples A and B points to slight changes in pyramidal Si─O bond angles, which increase the $3s$ contribution in the orbital of unpaired electron. The 7.4 mT doublet is due to the well-known "H(I)"-center. It is caused by hfc of unpaired electron of a dangling Si bond with proton in Si─H bond, substituting one of the three bridging Si─O bonds in the E' center [15].

The 10.5 mT doublet (Fig. 1, A, B, C, D, E) is present only in F-doped samples. Its intensity relative to the ^{29}Si hfc doublet grows with F content. To our knowledge, such signal has not been previously reported. The closest observation is the 10.0 mT doublet of "E'_δ" centers, assigned to the ^{29}Si hfc of electrons trapped on a cluster of 4 Si atoms [16]. However, it is observed only in oxygen-deficient glass, and the 0.5 mT difference in splitting would be well resolved in Fig. 1. Hence the 10.5 mT doublet is not related to E'_δ centers, and is very likely due to hfc with a ^{19}F nucleus.

The characteristic shape of the 10.5 mT doublet with its wide outer shoulders (Fig. 1, A) points to a center with an axially symmetric hfc tensor. To obtain a more accurate
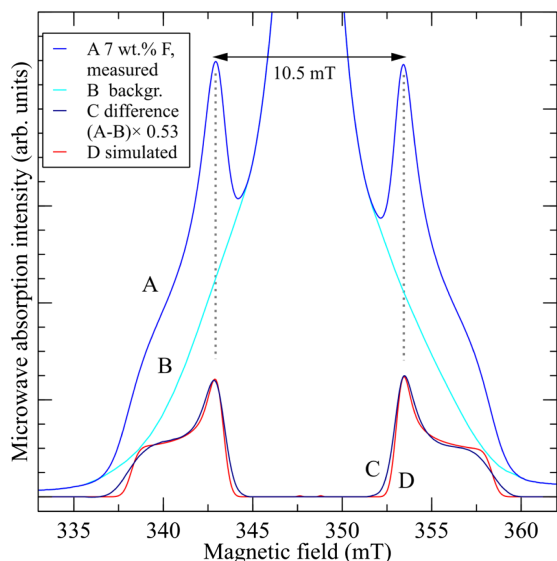
FIG. 2. Analysis of the 10.5 mT hyperfine doublet in 7 wt% F-doped silica. (A) measured spectrum, (B) putative background line, (C) difference "A"–"B", (D) computer-simulated spectrum, assuming isotropic $g = 2.0003$ and hyperfine coupling with $A_{\mathrm{iso}} = 375$ MHz, Gauss-distributed with FWHM = 43 MHz and $A_{\mathrm{aniso}} = 95$ MHz.
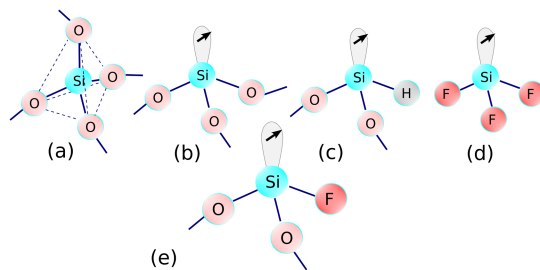

FIG. 3. Regular SiO_4 tetrahedron (a) in silica glass network and structures of paramagnetic dangling Si bond centers: generic E' center (b), $H(I)$ center (c), SiF_3 radical (d), and the proposed structure of $E'(\mathrm{F})$ center (e).

spectral shape (Fig. 2), a wide sloped background (B), drawn as an extension of the central line, was subtracted from the measured spectrum (A). The shape of the difference spectrum (C) was computer simulated with EasySpin software (Fig. 2, D), assuming an axial $^{19}\mathrm{F}$ hfc tensor. The doublet could be best simulated with close to isotropic g tensor ($g_1 \approx g_2 \approx g_3 = 2.0003 \pm 0.0005$), isotropic part of hyperfine tensor $A_{\mathrm{iso}} = 375$ MHz (13.4 mT), anisotropic part $A_{\mathrm{aniso}} = 95$ MHz (3.4 mT), and Gaussian distribution of A_{iso} with full width at half maximum FWHM = 43 MHz (1.53 mT). The simulation parameters were not sensitive to reasonable variations in selection of signal background (Fig. 2, B).

The obtained small g-tensor shifts from the free-electron value are similar to g shifts of different variants of E' centers in silica, all characterized by an unpaired spin in $3sp^3$-like dangling Si orbital. The well-resolved shape of 10.5 mT doublet lines in the measured spectrum points to a some quite definite position of the F nucleus relative to the unpaired electron wave function, despite the glassy disorder. In a silica glass random network, accurate interatomic distances and angles exist only within a single SiO_4 tetrahedron—or in a dangling Si bond originating from it. Based on this reasoning, the most probable position of the F atom giving 10.5 mT doublet is on the same pyramidal unit, where the dangling Si bond is located, i.e., when one of the three bridging Si—O—Si bonds is substituted by a Si—F bond. We denote this configuration as the "$E'(\mathrm{F})$" center, a silicon dangling bond on a Si atom, bonded by 2 bridging oxygens and by a fluorine atom (Fig. 3, e). This

configuration is akin to the well-known $H(I)$ center [15,17,18], featuring a Si—H bond (Fig. 3, c) and giving rise to the 7.4 mT doublet (Fig. 1 C, E, H, J).

Because of the large and similar electronegativities of F and O atoms, close characters of Si—F and Si—O bonding can be expected, much closer as compared to the Si—H bond in the $H(I)$ center. The Si—F and Si—O bond lengths are nearly identical ($\sim$160 pm). In this context, it is meaningful to compare the present results to the published [19,20] EPR properties of matrix-isolated SiF_3° radicals (Fig. 3, d). The g values (2.0003 vs 2.00028) and $^{19}\mathrm{F}$ hfc ($A_{\mathrm{iso}} = 13.4$ mT (our data) vs 13.64 mT) are closely similar in both cases. The anisotropic hfc for SiF_3, $A_{\mathrm{aniso}} = 4.49$ mT [20] is close to 3.4 mT, obtained by our simulation. The spot-on coincidence of A_{iso} is probably fortuitous, given the differences between Si—F and Si—O bond properties and the uncertainty in baseline applied to extract the form of $^{19}\mathrm{F}$ doublet (Fig. 2, B) used for simulation. Nevertheless, the close values show that the proposed structure of the $E'(\mathrm{F})$ center is well compatible with the measured magnitudes of $^{19}\mathrm{F}$ A_{iso} and A_{aniso}.

The magnitude of anisotropic hfc (3.4 mT) in "point dipoles" model corresponds to a distance of 92 pm between electron and fluorine nucleus, shorter than Si—F bond (158 pm). While this is an oversimplification, it indicates that F is close to unpaired electron distribution. More accurate character of F hfc (direct overlap, spin polarization...) can be given by quantum chemistry calculations, which, to our knowledge, do not yet exist.

The feature, common to all "dangling Si-bond"-type centers (Fig. 3 b, c, d), is the unpaired electron in a silicon sp^3-like orbital. It gives rise to low-intensity $^{29}\mathrm{Si}$ hyperfine doublets with respective splittings 42–44 [8], 31 [15], and 49.8 [19] or 52.3 mT [20]. A similar hyperfine feature should exist for the proposed structure of $E'(\mathrm{F})$ centers (Fig. 3, e) too.

The spectra of F-doped samples (Fig. 1) show $^{29}\mathrm{Si}$ doublet of "normal," not fluorine-related E' centers (Fig. 3, b) with 43 mT splitting, which decreases to 42 mT at lower F concentrations and in fluorine-free samples. A closer scrutiny reveals additional low-intensity
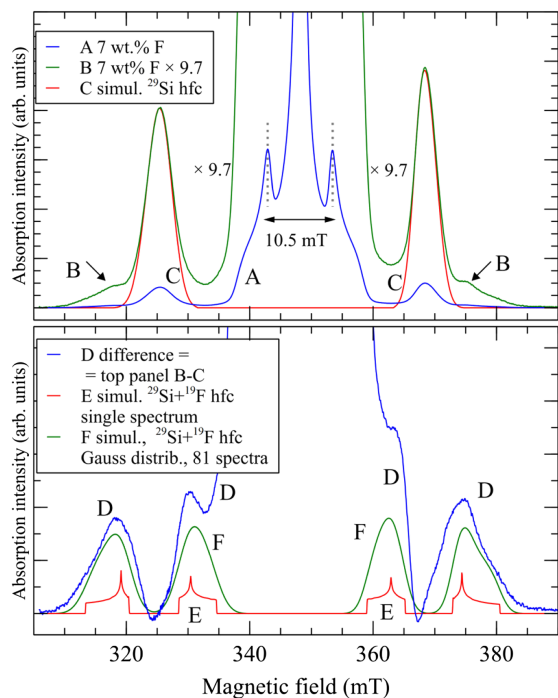
FIG. 4. Top panel: Details of the 43.0 mT hyperfine doublet in F-doped sample "*A*" (traces *A*, *B*). Slanted arrows point to the additional shoulders, not present in fluorine-free samples. Trace *C* is ^{29}Si hyperfine coupling computer simulation of E' centers, not related to fluorine. Bottom panel: Difference between the measured spectrum and simulated E' center ^{29}Si hfc contribution (trace *D*); simulated spectrum corresponding to combined ^{29}Si and ^{19}F hfc (trace *E*); the same simulated spectrum, assuming Gaussian distribution of the isotropic part of ^{29}Si hfc (trace *F*).

outer shoulders to ^{29}Si doublet lines in the F-doped sample (Fig. 4, *A*, *B*). They are not present in fluorine-free samples. To isolate their spectral shape, first, the 43 mT doublet in 7 wt.% F-doped sample ("*A*") was simulated, using $g_1 = 2.0003$, $g_2 = 2.0006$, $g_3 = 2.0017$, $A_{\text{iso}}(^{29}\text{Si}) = 1205$ MHz (43.0 mT) $A_{\text{aniso}}(^{29}\text{Si}) = 62$ MHz (2.2 mT), and assuming Gaussian distribution of $A_{\text{iso}}(^{29}\text{Si})$ with fwhm = 202 MHz (7.2 mT). Only $A_{\text{iso}}(^{29}\text{Si})$ was adjusted, its fwhm and $A_{\text{aniso}}(^{29}\text{Si})$ values were set to the published ones [8]. The simulated spectrum (Fig. 4, *C*) was subtracted from the measured spectrum, revealing 2 doubletlike structures centered on ~325 and 370 mT (Fig. 4, *D*). It must be noted, however, that the positions of the inner peaks of both doublets could be inaccurate, since they are sensitive to inaccuracies in background subtraction.

The difference spectrum (Fig. 4, *D*) was simulated (Fig. 4, *E*, *F*) assuming hfc both with ^{19}F and ^{29}Si nuclei. The ^{29}Si *A*-tensor parameters and their statistical distribution were taken over from those used to simulate the 43 mT doublet (Fig. 4, *C*), only the peak value of $A_{\text{iso}}(^{29}\text{Si})$ Gaussian distribution was adjusted to 1245 MHz (44.4 mT) during fitting. The ^{19}F hfc tensor was set to values determined from Fig. 2, apart from not applying

Gaussian distribution to $A_{\text{iso}}(^{19}\text{F})$, since its FWHM (1.53 mT) is small relative to the $A_{\text{iso}}(^{29}\text{Si})$ distribution (7.2 mT). The best fit was achieved when the Euler angle β between the axes of ^{29}Si and ^{19}F hyperfine tensors was set at ~45°. The shape of hyperfine doublets calculated using only a single value, corresponding to the peak of $A_{\text{iso}}(^{29}\text{Si})$ distribution (1245 MHz, 44.4 mT), is shown in Fig. 4, *E*. Trace "*F*" shows the hyperfine doublet shape, calculated as weighted average of 81 spectra, over the Gaussian distribution of $A_{\text{iso}}(^{29}\text{Si})$ within range ±2.5 FWHM from the center value. Here the most important is the fit to the outer doublet peaks of the measured spectrum, since the inner peak positions can be less accurate, as mentioned above.

The reasonably good fit of the measured spectrum (Fig. 4, *D*, *F*), achieved by using ^{19}F hfc parameters obtained from the fit to the 10.5 mT doublet (Fig. 2), confirms that the outer shoulders in the spectrum of F-doped silica (Fig. 4, *A*, *B*) are due to combined ^{29}Si and ^{19}F hfc; the magnitude of the ^{29}Si hfc (44.4 mT) is similar to that of E' centers and, by inference, indicates an unpaired electron in sp^3-like silicon orbital. Together with the good agreement between the measured ^{19}F hyperfine coupling and that reported for SiF$_3^\circ$ radicals [19,20] this supports the proposed model of $E'(\text{F})$ centers (Fig. 3, e): a dangling silicon bond, neighbored by a Si—F bond and 2 bridging oxygen atoms, projecting into the interstitial void of a silica glass random network.

The ratio between the sums of the integral intensities of the outer hyperfine (^{29}Si + ^{19}F) doublet lines (Fig. 4, D) and integrals of the fitted ^{29}Si lines (Fig. 4, C) is 0.19, which yields a ratio of 0.38 between the concentrations of $E'(\text{F})$ and the intrinsic E' centers. This indicates that $E'(\text{F})$ centers are not minor species, and play a significant role in radiation processes in strongly F-doped silicas. Further studies are necessary to elucidate their optical properties, important for photonics applications. The presently available data indicate that they, similarly to E' centers, have no photoluminescence, but their optical absorption band is most likely shifted to shorter wavelengths relative to the 215 nm band of E' centers.

Conclusion.—An important problem, concerning multiple applications of F-doped silica in optical fibers and elements is the mechanisms of defect creation in this radiation-tough optical material. The new point defect, identified in this Letter indicates that, in addition to the two well-known fundamental mechanisms for the creation of dangling Si bonds (E' centers) in silica: by creating oxygen vacancies, and by breaking strained Si—O bonds [21], an energetically less demanding process, compared to oxygen vacancy creation, could be the displacement or radiolysis of a F atom at sites of the SiF$_2$ bonds [5]:

$$(-\text{O}-)_2\text{Si-F}_2 \rightarrow (-\text{O}-)_2\text{Si}^\circ\text{-F} + \text{F}^\circ.$$
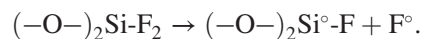
The present Letter provides evidence for this reaction by identifying its right-side product. It is of interest to prove if this reaction contributes to the observed increase ([5] and Refs. therein) of the radiation damage in fluorine-doped silica, when fluorine concentration exceeds 0.1 wt.%. The ^{19}F nuclear magnetic resonance (NMR) studies [22–24] still do not provide a unanimous picture of the additional fluorine incorporation forms in silica, different from the monofluoride $(-O-)_3Si-F$ bonds. Observations of $(-O-)_2SiF_2$ groups are confirmed [22,24] or rejected [23]. Configurations with fivefold coordinated Si coordinated by 4 bridging oxygens and fluorine atoms are inferred by NMR [23,24] and by molecular dynamics study [1]. Fluorine at such sites should be less stable than in SiF groups at fourfold coordinated Si, and should contribute to radiation damage. Quantum chemistry-based evaluations of these processes do not exist. We believe that the identification of $E'(F)$ centers will help to understand radiation processes in this radiation-tough optical glass.

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