Structure and paramagnetic properties of defect centers in Ge-doped SiO_2 glass: Localized and delocalized Ge E' centers

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We have presented a new structural model of the hole-trapping oxygen deficient center in Ge-doped silica glass on the basis of *ab initio* molecular orbital calculations. This charged center comprises the hole ($\equiv Ge^+$ or $\equiv Si^+$) and the paramagnetic ($\equiv Ge\bullet$) parts that are bridged by a common oxygen atom. The isotropic ^{73}Ge hyperfine coupling calculated for this paramagnetic center reproduces the observed value better than that obtained for the triplet-state delocalized center proposed in a previous paper [T. Uchino *et al.*, Phys. Rev. Lett. **84**, 1475 (2000)].

One of the interesting applications of silica-based materials is the production of modulated refraction index patterns by defect photoconversion in Ge-doped SiO_2 glass.[1] Among other defects in Ge-doped SiO_2 glass, divalent Ge defects, which are coordinated to two oxygen atoms in their first coordination sphere and yield ~5 eV photoabsorption band,[2] have received recent interest since they are believed to play a vital role in modifying the physical and optical properties of the materials upon high-power density ultraviolet (uv) irradiation such as ArF and KrF excimer lasers.[3] The 5 eV absorption band is appreciably bleached by high-power density uv irradiation,[4] generating several paramagnetic defects associated with Ge atoms.[5] A principal photoinduced paramagnetic defect is the Ge E' center having an unpaired electron localized in a dangling sp^3 orbital of a three-coordinated Ge atom. However, only little is known about the formation mechanism of the Ge E' center from Ge divalent defects, and the related photoinduced phenomena observed for Ge-doped SiO_2 glasses are not fully understood yet at the atomic scale level.

In a recent paper,[6] we have proposed a novel mechanism of the photoinduced conversion of a divalent Ge defect to Ge E' centers on the basis of quantum chemical calculations on clusters of atoms modeling the local structure of the relevant defects in Ge-doped SiO_2 glass. A brief summary of the proposed mechanism is as follows. Irradiation with the high-power uv laser excites one of the lone pair electrons on a divalent Ge defect to the conduction band, giving rise to a positively charged Ge center. This charged center attracts one of the neighboring bridging oxygen atoms to form three-coordinated O and Ge atoms [model 1(+), see Fig. 1]. As a result of the subsequent electron-hole recombination, the atomic configurations around so formed defects are rearranged, forming a triplet-state defect consisting of two unpaired spins delocalized over the dangling sp^3 orbitals of the two Ge atoms [model 1(*T*), see Fig. 1].

Such a triplet-state defect is indeed observed in irradiated pure SiO_2 glass,[7,8] and, therefore, its analogue is expected to exist in Ge-doped SiO_2 glass as well. However, the triplet-state Si defect may be characterized by a small ^{29}Si hyperfine splitting, *A*, as compared with the major paramagnetic defect called the Si E'_γ center because of the spin delocalization. This suggests that the above triplet-state model is not responsible for the observed main ^{73}Ge hyperfine splitting of ~24 mT in Ge-doped SiO_2 glass[9,10] since the ~24 mT splitting is likely due to the ''localized'' Ge E' center analogous to the Si E'_γ center.[11] In this paper, we, therefore, carry out further quantum chemical calculations on germanosilicate clusters in order to give a theoretical explanation for the electron paramagnetic resonance (EPR) characteristics observed for Ge-doped SiO_2 glass. We then propose a formation mechanism of the ''localized'' Ge E' center from the divalent Ge and other defect centers.

The conventional model of the Si E'_γ center was given by Feigl, Fowler, and Yip, FFY;[12] that is, a neutral oxygen monovacancy in silica will show an asymmetric relaxation by trapping a positive hole, leading to a defect structure, $\equiv Si^+ \bullet Si \equiv$, where $\equiv$ and $\bullet$ represent the three Si-O bonds and the unpaired electron, respectively. Since a similar mechanism was suggested for the formation of the Ge E' center in Ge-doped silica glass,[13] we first tried to obtain the optimized geometry of the paramagnetic defect center on the basis of the FFY model. The $Ge_3Si_2O_{15}H_{12}$ cluster (model 2) that models a neutral oxygen monovacancy is shown in Fig.

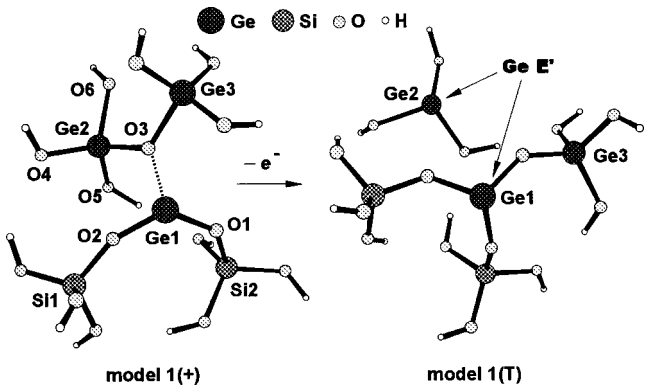

FIG. 1. Previously proposed formation mechanism of a triplet-state defect in Ge-doped silica glass (Ref. 6). A $(Ge_3Si_2O_{15}H_{12})^+$ cluster modeling a positively charged divalent Ge defect [left, model 1(+)], which attracts an adjacent bridging oxygen to form a three-fold coordinated Ge atom (Ge1), transforms into a triplet-state defect [right, model 1(*T*)] having two equivalent Ge E' centers via hole-electron recombination.

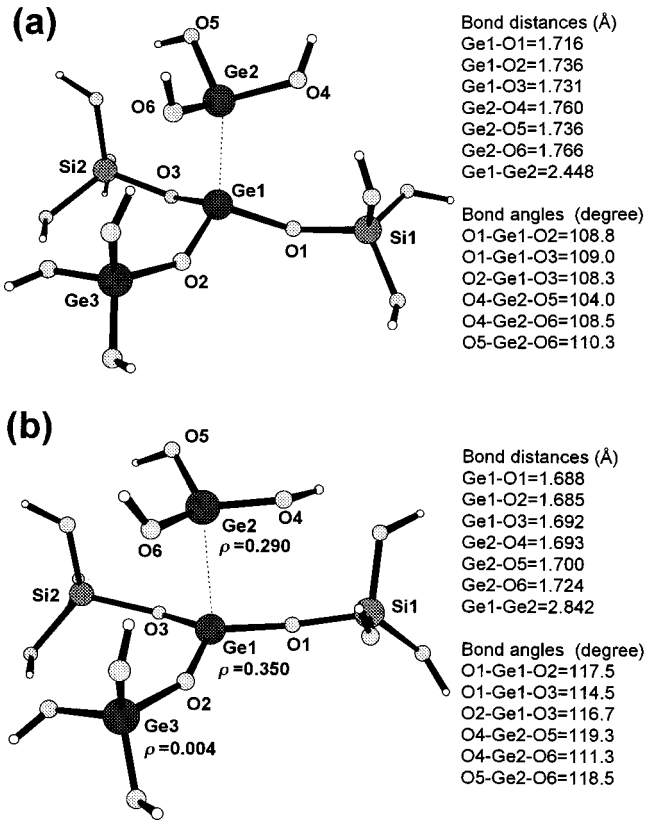

FIG. 2. $Ge_3Si_2O_{15}H_{12}$ cluster models of (a) a neutral (model 2) and (b) a positively charged [model 2(+)] oxygen monovacancies fully optimized at the (U)HF/6-311$G(d)$ level. The calculated structural parameters and charge densities ρ are also shown.

2(a). The dangling bonds of the ''surface'' oxygen atoms are saturated by H atoms, and the full geometry optimization was then carried out by assuming a total charge of +1 for model 2 [$(Ge_3Si_2O_{15}H_{12})^+$, model 2(+)] at the unrestricted Hartree-Fock (UHF) level using the 6-311$G(d)$ basis set.[14] All the *ab initio* quantum chemical calculations in this work were performed using the GAUSSIAN98 program[15] on a supercomputer CRAY T94/4128.

As a result of the geometry optimization of model 2(+), however, we did not obtain the configurations of the conventional defect model proposed by FFY. The resultant geometry is rather symmetric and the unpaired electron is delocalized over the two Ge atoms of the vacancy [see Fig. 2(b)],[16] which is inconsistent with the localized nature of the Ge E' center. Table I shows the ^{73}Ge hyperfine constants calculated for the Ge atoms in model 2(+). One sees from Table I that all the Ge atoms in model 2(+) are characterized by rather weak hyperfine splittings, indicating that this ''delocalized'' paramagnetic center does not account for the main EPR characteristics in Ge-doped silica glass.

The optimized configurations of the FFY-type defect were previously reported by several researchers.[17–20] In these studies, the charged vacancy was created in the α-quartz-type lattice since the FFY model was originally proposed for the paramagnetic defect center in such a crystalline form of silica. Indeed, constraints from the surrounding crystalline lattice enable one to obtain the asymmetrical relaxation of the charged oxygen vacancy, which will be stabilized further by forming a puckered configuration of the $\equiv Si^+$ unit.[17] In

TABLE I. ^{73}Ge isotropic hyperfine coupling constants, in mT, calculated for the different defect models at the UHF/6-311$G(d)$ level along with the experimental value obtained for the Ge E' center in Ge-doped silica glass.

	Model			
	Model 1(T)	Model 2(+)	Model 3(+)	Experiment[a]
Ge1[b]	10.88	2.99	23.21 (23.17[c])	23.8
Ge2[b]	9.82	1.46	0.32	
Ge3[b]	0.08	0.02	0.00	

[a]Reference 10.

[b]For atom labels, see Figs. 1–3

[c]The UHF/6-311$G(d)$ value calculated for the optimized cluster in which all of the Ge atoms except Ge1 in model 3(+) were replaced by Si atoms.

noncrystalline silica-based materials, however, such structural constraints may not exist, and the flexibility of the amorphous network will allow the structural rearrangements not only in the defect site of interest but in its more remote coordination spheres. It is hence probable that even if the charged oxygen monovacancy is formed in the amorphous network, this charged center will not necessarily show the asymmetrical relaxation as in the case of α-quartz but may tend to result in the dimer configuration as shown in Fig. 2(b). It should be noted, however, that one does not even observe EPR signals associated with the delocalized paramagnetic center that can be found in model 2(+). This suggests that such a charged defect as seen in model 2(+) is highly unstable against electron-hole recombination. Indeed, the atomic configurations of the charged oxygen monovacancy shown in Fig. 2(b) is nearly the same as those of its neutral precursor shown in Fig. 2(a). In other words, this positively charged paramagnetic defect will be very easy to relax into a stable neutral state just by trapping an electron, explaining the absence of the delocalized Ge hyperfine interactions in the experimental EPR spectra. Taking these things mentioned above into account, we suggest that the FFY model along with the conventional oxygen monovacancy will not fully account for the microscopic origin of the E' centers in silica-based materials.

To give a microscopic explanation of the localized Ge E' center in Ge-doped silica glass, we here propose another configuration of the charged defect center, which will be referred to as model 3(+). The geometry of model 3(+) was fully optimized at the UHF/6-311$G(d)$ level, and the resultant configuration is depicted in Fig. 3. The total energy of model 3(+) was found to be lower than those of models 1(+) and 2(+) by 0.14 and 1.57 eV, respectively, indicating that the atomic configuration of model 3(+) is the most stable among the positively charged $(Ge_3Si_2O_{15}H_{12})^+$ clusters employed. Model 3(+) consists of two types of three-coordinated Ge units that are bridged by a common oxygen atom (O3), forming an asymmetrical charge trapping center. It is clear from Fig. 3 that the spin density ρ in model 3(+) is mainly localized at one of the two $\equiv$Ge units ($\rho_{Ge1}=0.841$) of the defect, indicating that the paramagnetic $\equiv$Ge unit has a nearly isolated dangling bond of sp^3 character. The other $\equiv$Ge unit in model 3(+) has substantially no spin density at the Ge site ($\rho_{Ge2}=0.010$), yielding an almost planar $\equiv Ge^+$ structure.

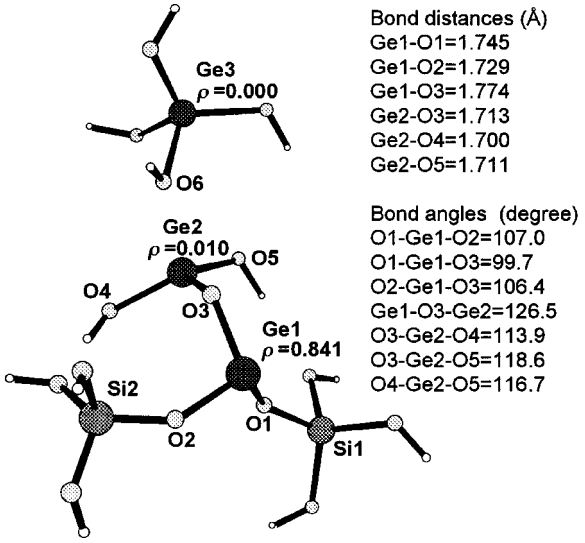

FIG. 3. The lowest energy configuration among the positively charged $Ge_3Si_2O_{15}H_{12}$ clusters employed [model 3(+)]. The geometry was fully optimized at the UHF/6-311$G(d)$ level. The calculated structural parameters and charge densities ρ are also shown.

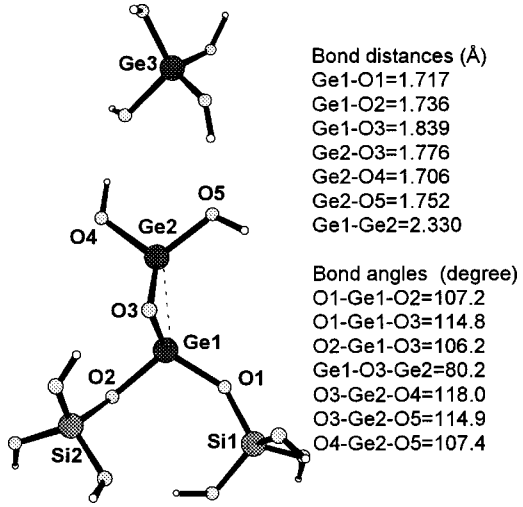

FIG. 4. A $Ge_3Si_2O_{15}H_{12}$ cluster model (model 3) derived from model 3(+). The geometry was fully optimized at the HF/6-311$G(d)$ level.

Thus, in model 3(+), the paramagnetic part of the defect ($\equiv$Ge1) is quite isolated from the hole part ($\equiv$Ge2) and behaves much like a trapped electron similar to the case of the FFY model.

It is interesting to calculate the hyperfine parameters for the defect center in model 3(+). As expected from the spin densities, the strong hyperfine coupling can only be found in Gel (see Table I), and the calculated value ($\mathbf{A}_{\mathrm{Gel}}^{\mathrm{cal}} = 23.21\,\mathrm{mT}$) is in excellent agreement with the experimental ^{73}Ge hyperfine coupling observed for the GeE' center in Ge-doped silica glass ($\mathbf{A}^{\mathrm{exp}} = 23.8\,\mathrm{mT}$[10]). We have also confirmed that the hyperfine coupling calculated for Ge1 in model 3(+) is basically unchanged even if Ge2 and Ge3 atoms are replaced by Si atoms ($\mathbf{A}_{\mathrm{Gel}}^{\mathrm{cal}} = 23.17\,\mathrm{mT}$, see Table I). This indicates that the electronic structure of the paramagnetic part of the defect ($\equiv$Ge1$\bullet$) is hardly affected by the type of atoms in its adjacent hole part ($\equiv Ge^+$ or $\equiv Si^+$). On the other hand, the paramagnetic Ge atoms in model 1(T) yield much weaker hyperfine splittings than Ge1 in model 3(+) (see also Table I). Thus, the present calculations suggest that this newly proposed defect center can be a suitable candidate for the GeE' center in Ge-doped silica glass. We should also note that models 1(+) (see Fig. 1) and 3(+) have the same stoichiometry of $(Ge_3Si_2O_{15}H_{12})^+$, and, therefore, an interconversion between the two configurations is, in principle, possible to occur; such an interconversion will be accomplished just by creating a new bond between Ge3 and O6 atoms in model 1(+) at the expense of the original Ge3-O3 and Ge2-O6 bonds.

We can then create a neutral singlet-state oxygen vacancy by adding one electron to model 3(+). The HF/6-311$G(d)$ geometry of the resulting neutral cluster (model 3) is shown in Fig. 4. Although the defect center in model 3, which will be referred to as a triangular oxygen defect center (TODC) from its geometrical configuration, is rather different from the conventional oxygen vacancies, the present calculations elucidate that the formation of this new type of oxygen vacancy is energetically feasible. It is reasonable to expect that model 3 can also be transformed into the hole-trapping center, model 3(+), implying that the TODC as well as the Ge divalent defect can be a precursor of the newly proposed GeE' center yielding the $\sim 24\,\mathrm{mT}$ ^{73}Ge hyperfine splitting. We have recently demonstrated that TODC consisting of two Si atoms is also expected to exist in pure SiO_2 glass, and this Si analogue converts into an asymmetric paramagnetic center as seen in model 3(+).[21]

Nishii *et al.*[5] have confirmed that there exist at least two independent photoinduced reaction channels that yield the GeE' centers in the glasses. One is the two-photon process, which is caused by the high-power density irradiation with ArF and KrF excimer lasers and will be related to the photochemical reactions of the Ge divalent defect as mentioned repeatedly in this paper. The other is the one-photon process, which proceeds upon the low-power density irradiation with, for example, a Hg discharge lamp. As a mechanism for the one photon process, the following reaction was suggested:[5,13] $\equiv Ge{-}Ge\equiv \xrightarrow{uv} \equiv Ge^+ + \bullet Ge\equiv + e^-$. We have, however, demonstrated earlier that this reaction associated with a neutral oxygen monovacancy is not likely to occur in Ge-doped silica glass. Instead, we have proposed a photoinduced conversion from the TODC to the GeE' center. Since exposure to Hg lamp radiation bleaches the optical absorption band near 5 eV,[5,13] which (accidentally) lies very close to the band attributed to the Ge divalent defect, the defect center yielding the $\sim$5 eV band will be responsible for the one photon process. We hence calculate the excitation energies of the TODC using the time-dependent density-functional response theory[22] (TD DFRT), which has been found to be an efficient method to obtain reasonable electronic excitation spectra of relatively large molecules.[23] The TD-DFRT excitation energies were calculated for the HF/6-311$G(d)$ geometry of model 3 at the Becke's 1993 hybrid exchange functional with the Lee-Yang-Parr correlation energy functional[24] (B3LYP) level with the 6-311$G(d)$ basis set augmented by two sets of diffuse s and p functions on the two Ge atoms in TODC. The first singlet-to-singlet excitation ($S_0 \rightarrow S_1$) energy of model 3 was calculated to be 4.70 eV. When we

replace one of the Ge atoms in TODC by a Si atom, the resultant HF/6-311$G(d)$ optimized cluster yields the TD–DFRT excitation energy of 5.25 eV. These calculated excitation energies are in reasonable agreement with the absorption energy of the bleachable band (~5.0 eV), supporting the conversion mechanism from the TODC to the Ge E' center.

In conclusion, we have presented a new structural model of the charged defect center in Ge-doped silica glass on the basis of *ab initio* quantum chemical calculations. This charged center consists of the paramagnetic ($\equiv$Ge•) and hole ($\equiv Ge^+$ or $\equiv Si^+$) parts that are bridged by a common oxygen atom. The isotropic hyperfine coupling calculated for the paramagnetic part in this defect center quantitatively reproduce the observed ~24 mT splitting, whereas the triplet-state center proposed previously[6] yields much weaker (~10 mT) hyperfine couplings. The divalent Ge defect and the TODC (see Fig. 4), which will both contribute to the ~5 eV photoabsorption band, can be independently transformed into this newly proposed paramagnetic defect. We believe the present scenario will cast new light on the observed photochemical reactions in Ge-doped silica glass induced by one- and two-photon absorption processes.

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