# Calculated spectral properties of self-trapped holes in pure and Ge-doped SiO<sub>2</sub>

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We report first-principles cluster model calculations on the electronic structure and spectral properties of self-trapped holes (STH's) in pure and Ge-doped silica. Two different kinds of STH's are considered: STH<sub>1</sub>, consisting of a hole trapped at the 2p nonbonding orbital of an O atom bridging two Si atoms, and STH<sub>2</sub>, a metastable defect where the hole is rapidly tunneling between two adjacent O atoms that we modeled by a hole delocalized over two bridging O atoms. The computed hyperfine coupling constants for the two variants of STH centers fully support the experimental assignments based on the analysis of the electron spin resonance spectra. We also considered the lowest optical transitions of these defect centers, and we compared the results with the experimental bands observed in irradiated quartz and with the position of the energy levels deduced from the analysis of the g matrices. [S0163-1829(99)02838-6]

#### I. INTRODUCTION

One of the most fundamental point defects in insulators is the self-trapped hole (STH). In crystals self-trapped holes are referred to as "polarons," indicating a highly localized carrier in the material. When the spatial extent of the carrier wave function is smaller than the lattice constant, one speaks of "small polarons." The best characterized example of a polaron in a crystal is the  $V_k$  center in alkali halides, consisting of a hole shared between two neighboring halide anions which relax to decrease their distance. A similar process can occur in glasses and disordered structures. Understanding the nature of charge traps in amorphous SiO<sub>2</sub>, *a*-SiO<sub>2</sub>, is of fundamental importance for the fabrication of radiationtolerant metal-oxide semiconductor devices.

Self-trapping in silica was predicted by Mott 20 years ago.<sup>1</sup> It is only in the last decade that STH's in SiO<sub>2</sub> have been observed through spectroscopic measurements. Hayes and Jenkin<sup>2</sup> used electron spin resonance (ESR) to identify a defect center in Ge-doped  $\alpha$ -quartz assigned to a hole completely localized on a oxygen atom bridging a Si and a Ge atom. This defect was not observed by the same group in undoped  $\alpha$ -quartz. This was attributed to the fact that in crystalline quartz the hole hopping rate is too fast to allow ESR detection even at 4 K. Since activation energies of the order of 0.1-0.4 eV have been estimated for hole transport in a-SiO<sub>2</sub>, better prospects for spectroscopic detection of STH's in silica have been anticipated. Indeed, in two separate experiments, Griscom<sup>3</sup> and Chernov et al.,<sup>4</sup> respectively, reported ESR and optical observations of STH's in a-SiO<sub>2</sub>. Griscom<sup>3,5</sup> identified two species of STH's, STH<sub>1</sub> and STH<sub>2</sub>, characterized by different g values and hyperfine coupling constants (hfcc's). It has also been observed that lowtemperature irradiation of Ge-doped quartz leads to two absorption peaks at 2.25 and 4.2 eV tentatively assigned to small hole polarons bound at oxygen sites.<sup>6</sup>

From the theoretical point of view, only two studies have been reported on this problem. Chernov *et al.*<sup>4</sup> performed semiempirical cluster calculations on the nature of a STH in a-SiO<sub>2</sub> and concluded that the hole is delocalized over all the oxygen atoms of the cluster. More recently, Edwards<sup>7</sup> reported both semiempirical and ab intio Hartree-Fock calculations on a cluster model and concluded, at variance with the results of Chernov et al.,<sup>4</sup> that the hole is completely localized on a bridging oxygen atom. The conclusion of Edwards is supported by the agreement obtained in the comparison of measured<sup>6</sup> and computed<sup>7</sup> hfcc's. No attempt, however, has been done to characterize the electronic structure of both STH<sub>1</sub> and STH<sub>2</sub> as observed by Griscom<sup>5</sup> or to compute the optical excitations of STH's. Furthermore, the previously reported calculations<sup>4,7</sup> refer to pure silica and do not include any treatment of electron correlation. For all these reasons we decided to investigate in more detail the nature of holes trapped in pure and Ge-doped silica. To this end we performed ab initio quantum chemical calculations based on cluster models. Particular attention has been paid to the reproduction of spectral features, in particular the ESR parameters and the optical transitions associated with STH's in silica.

## **II. COMPUTATIONAL METHOD**

The structures of STH's in silica have been represented two cluster models. In the smaller by one. (HO)<sub>3</sub>Si-O-Si(OH)<sub>3</sub>, Fig. 1(a), there is only one O atom which is properly coordinated to two Si atoms [or to a Si and a Ge atom, for the case of Ge-doped silica, Fig. 1(b); in the larger cluster, [(H<sub>3</sub>Si)-O]<sub>4</sub>Si, Fig. 1(c), four bridging O atoms are present. This second cluster is also used to model a hole delocalized over two O centers. For brevity, in the following the two clusters are denoted as cluster A and cluster B, respectively. The cluster dangling bonds have been saturated by H atoms, a commonly used technique to "embed" clusters of semiconducting or insulating materials.<sup>8</sup> The positions of the cluster atoms were initially fixed to those of  $\alpha$ -quartz derived from x-ray diffraction data at 94 K.<sup>9</sup> The embedding H atoms were fixed at a distance of 0.96 Å from the respective O atoms (cluster A) or at 1.48 Å from the Si

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FIG. 1. Cluster models of a self-trapped hole in pure and Gedoped silica. (a) Cluster A, model of STH<sub>1</sub> in  $\alpha$ -quartz; (b) cluster A, model of STH<sub>1</sub> in Ge-doped  $\alpha$ -quartz; and (c) cluster B, model of STH<sub>1</sub> and STH<sub>2</sub> in  $\alpha$ -quartz.

atoms (cluster *B*) along the O-Si directions of  $\alpha$ -quartz. The positions of all the Si and O atoms of the cluster have been fully optimized. The fixed H atoms provide a simple representation of the mechanical embedding of the solid  $\alpha$ -quartz matrix. The same approach has been recently adopted for the study of the ground- and excited-state properties of other defects in silica.<sup>10-16</sup>

The cluster wave functions have been constructed using local Gaussian-type atomic orbital basis sets. The Si and Ge atoms have been treated either at the all-electron (AE) level or by using effective core potentials (ECP's) which include explicitly in the valence only the  $ns^2np^2$  electrons.<sup>17,18</sup> For Ge a relativistic ECP has been used.<sup>18</sup> The [4s4p/2s2p] ECP basis sets<sup>17,18</sup> on Si and Ge were augmented by a *d* polarization function  $[\alpha_d(Si)=0.395, \alpha_d(Ge)=0.15]$  and by one set of diffuse s and p functions ( $\alpha_{Si}=0.035$ ,  $\alpha_{Ge}$ =0.040). AE 6-31G or 6-31G\* (Ref. 19) and MINI-1 (Ref. 20) basis sets were used on the O and terminating H atoms, respectively. The validity of the ECP has been tested by comparing the results with those of AE calculations with Si and Ge basis sets of comparable size for the valence part; in particular, we used a 6-31G\* basis set on Si,19 and an eventempered (ET) [17s13p8d/6s5p2d] (Ref. 21) AE basis set on Ge. These basis sets contain or have been augmented by diffuse s, p, and one d polarization functions with similar

exponents to those used with the ECP basis sets. The differences in the geometry due to the basis set or to the ECP are negligible. Geometry optimizations have been performed at the restricted and unrestricted Hartree-Fock (RHF or UHF) levels for singlet closed-shell and doublet open-shell states, respectively, by computing analytical gradients of the total energy. Given the low local symmetry of the defect in quartz, the clusters are computed without any symmetry element ( $C_1$  symmetry group). However, in order to facilitate the description of a hole delocalized over two O atoms, clusters with  $C_2$  symmetry have also been constructed. These have been obtained by simply taking one-half of the cluster derived from the structure of  $\alpha$ -quartz and by generating by symmetry the second part. This procedure leads to clusters which are structurally different from the  $C_1 \alpha$ -quartz clusters, but the electronic properties considered, in particular the hyperfine coupling constants, are practically independent of the symmetry used (see below).

The hyperfine interactions of the electron spin in STH's with the nuclear spin of the <sup>1</sup>H, <sup>17</sup>O, <sup>29</sup>Si, and <sup>73</sup>Ge nuclides have been determined from UHF wave functions. The hyperfine interaction is anisotropic, and the **A** tensor is composed of two terms. The first one,  $a_{iso}$ , is related to the isotropic Fermi contact term and depends on the electron density of an *s* electron at the nucleus according to

$$a_{\rm iso} = (8\pi/3)g_N\beta_Ng_e\beta|\Psi_s(0)|^2, \qquad (1)$$

where  $g_N$  and  $g_e$  are the nuclear and electronic g factors and  $\beta_N$  and  $\beta$  are the nuclear and Bohr magnetons. The second term of the **A** tensor is a 3×3 traceless matrix **B**, which represents the "classical" dipolar interaction between two magnetic (electron and nuclear) moments. Typical anisotropic interactions can be observed when the unpaired electron is in directional orbitals like p, d, f, etc. The **A** tensor can therefore be represented by the following matrix notation:

$$\mathbf{A} = \begin{vmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{vmatrix} = a_{\rm iso} + \begin{vmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_3 \end{vmatrix}.$$
(2)

We have determined both isotropic and dipolar parts of the interaction from fully optimized structures.

The calculations of electronic excitations require the explicit treatment of correlation effects. These have been included by performing multireference single- and doubleexcitation configuration interaction (MRSD CI) calculations for the ground and excited states of the clusters.<sup>22,23</sup> Single and double excitations with respect to more than one reference or main configuration (M) are generated; in this way, it is possible to include directly higher-excitation classes with respect to the leading configuration in the final CI results. The method makes use of an extrapolation technique; only those configurations with an estimated contribution to the total CI energy larger than a given threshold T are included in the secular determinant; the contribution to the final CI energy of the remaining configurations is estimated perturbatively based on an extrapolation technique. Twenty-five valence electrons have been correlated for each Si- or Gecontaining cluster model of STH's. Typically, a few thousand configurations are directly included in the secular

Method	Symmetry	r(Si-O) <sub>1</sub> , (Å)	r(Si-O) <sub>2</sub> , (Å)	r <sub>av</sub> (Si-O) <sup>b</sup> (Å)	$\alpha$ (Si-O-Si)	$\beta$ (O-Si-O) <sup>b</sup>
		α-	-quartz, ≡Si—0	0—Si≡		
AE	$C_1$	1.625	1.632	1.630	148°	109°
AE	$C_2$	1.627	1.627	1.638	146°	109°
ECP	$C_2$	1.616	1.616	1.624	147°	109°
		S	$TH_1$ , $\equiv Si = 0^+$	⁺—Si≡		
AE	$C_1$	1.817	1.793	1.586	139°	102°
AE	$C_2$	1.835	1.835	1.590	135°	103°
ECP	$C_2$	1.787	1.787	1.574	150°	102°

TABLE I. Computed geometrical parameters of  $\alpha$ -quartz and STH<sub>1</sub> centers.<sup>a</sup>

<sup>a</sup>Results obtained with cluster A; see Fig. 1(a).

<sup>b</sup>Average value.

problem, while the number of generated configurations can be  $1-10 \times 10^6$ . The reported CI energies are extrapolated to this larger CI space. All configurations contributing more than 0.1% to the final CI wave function are used as main (*M*) configurations.

Absorption intensities have been estimated by means of the oscillator strength f, computed using the dipole-length operator as

$$f(\mathbf{r}) = 2/3 |\langle \psi_{e''} | e \mathbf{r} | \psi_{e'} \rangle|^2 \Delta E, \qquad (3)$$

where  $\Delta E$  is the calculated transition energy. The value of f for a fully allowed transition is of the order of 0.1–1. From the values of  $f(\mathbf{r})$  the expected lifetimes of the excited states,  $\tau$ , have also been determined.

The calculations have been performed using the HONDO-8,<sup>24</sup> GAUSSIAN 94,<sup>25</sup> and GAMESS-UK (Ref. 26) program packages.

### **III. RESULTS AND DISCUSSION**

#### A. Geometric and electronic structure

Before discussing the geometrical parameters of STH<sub>1</sub> and STH<sub>2</sub> centers in pure and Ge-doped silica as obtained from the present cluster calculations, we briefly comment on the geometry optimization of the nondefective clusters A and B, i.e., before the hole is created. The results have been obtained either by imposing a  $C_2$  symmetry on the system or for a structure derived from  $\alpha$ -quartz ( $C_1$  symmetry). The main difference is that in the  $C_1$  clusters the distances between the bridging oxygen atom  $O_1$  and the nearest Si atoms Si<sub>1</sub> and Si<sub>2</sub> are not equivalent, as in  $\alpha$ -quartz, while they are identical in the  $C_2$  clusters, Table I. For the neutral cluster A,  $\equiv$ Si-O-Si $\equiv$ , the Si-O distances are 1.625 and 1.632 Å in  $C_1$  and 1.627 Å in  $C_2$  (AE results); the Si-O-Si angle is  $147^{\circ} \pm 1^{\circ}$ . Very similar results are obtained by using an ECP on the Si atoms, Table I. These geometrical parameters are close to the experimental ones for  $\alpha$ -quartz, 1.614 and 1.605 Å and  $144^{\circ}$ .<sup>9</sup> The larger cluster *B* gives similar geometrical parameters, Table II and Fig. 1(c); also, the O-Si-O angles are close to those of the bulk material,  $\approx 109^{\circ}$ . The substitution of a Si atom by a Ge atom, Table III, leads to a O-Ge distance, 1.72 Å,  $\approx 0.1$  Å longer than the O-Si one. The Si-O-Ge angle, 138°, is slightly smaller than in pure silica.

Also in this case no significant difference is found between the AE and ECP results, Table III.

The geometry optimizations on the neutral clusters show a good agreement between theory and experiment and suggest that the local relaxation around a STH can be predicted with a sufficient level of accuracy. However, long-range relaxation effects due to the hole trapping cannot be included in a cluster model and can in principle lead to somewhat different local geometrical parameters. A STH<sub>1</sub> center has been obtained from cluster A by removing one electron. If this is done starting from the density of the neutral cluster, the hole tends to form on the O atoms directly bonded to the terminal H atoms and thus to be delocalized over the entire cluster. This result explains in part why Chernov et al.<sup>4</sup> have found such a solution for their models. If the calculation is performed from a cluster in  $C_2$  symmetry, however, it is possible to obtain a self-consistent field (SCF) solution where the hole is entirely localized on the central oxygen atom. Using the density from this latter calculation as a starting point, we have repeated the calculation on the  $C_1 \alpha$ -quartz model and we obtain a wave function where the unpaired electron resides on the central O atom. This is clearly shown by the spin population, Table IV. This shows that the formation of a localized hole does not come out automatically from the calculation. The same tendency has been found by Edwards;<sup>7</sup> in order to obtain a localized hole, the Si-O-H bond angles in his model have been distorted up to 170°, quite far from the value of 144° of  $\alpha$ -quartz.

In the ground state, the unpaired electron occupies a nonbonding 2p level of the central O atom. This 2p level is normal to the Si-O-Si plane and in  $C_2$  symmetry belongs to

TABLE II. Computed geometrical parameters of  $\alpha$ -quartz, STH<sub>1</sub>, and STH<sub>2</sub> centers.<sup>a</sup>

	$\alpha$ -quartz	$STH_1$	$STH_2$
$r(Si_1-O_1)$ (Å)	1.621	1.830	1.657
$r(Si_1-O_3)$ (Å)	1.628	1.570	1.578
$r(Si_2-O_1)$ (Å)	1.674	1.843	1.772
$\alpha(O_1-Si_1-O_2)$	106°	94°	84°
$\beta(Si_1-O_1-Si_2)$	153°	161°	168°
$\gamma(O_3-Si_1-O_4)$	109°	109°	116°

<sup>a</sup>Results obtained with cluster B in  $C_2$  symmetry: see Fig. 1(c).

Method	r(Si-O <sub>1</sub> ) (Å)	r(Ge-O <sub>1</sub> ) (Å)	r <sub>av</sub> (Si-O) (Å)	r <sub>av</sub> (Ge-O) (Å)	α(Si-O-Ge)	β(0-X-0)
		Ge-dop	ed $\alpha$ -quartz, $\equiv$	≣Si—O—Ge≡		
AE	1.619	1.717	1.636	1.732	138°	110°
ECP	1.620	1.714	1.615	1.733	140°	110°
		STI	$H_1(Ge), \equiv Si_{}$	$0^+$ —Ge $\equiv$		
AE	1.776	1.881	1.598	1.686	149°	103°
ECP	1.774	1.899	1.573	1.686	150°	102°

TABLE III. Computed geometrical parameters of the Ge-doped  $\alpha$ -quartz and STH<sub>1</sub> center in Ge-doped  $\alpha$ -quartz.<sup>a</sup>

<sup>a</sup>Results obtained with cluster A in  $C_1$  symmetry: see Fig. 1(b).

the *B* irreducible representation  $(2p_y)$ . This is indeed the ground state of STH<sub>1</sub> as found by Hayes and Jenkin<sup>2</sup> for Ge-doped silica. They have determined the *g* matrix of the Ge-pinned hole trap in quartz with absolute reference to the crystallography, and they found that the direction corresponding to the smallest principal-axis *g* value lies parallel to the direction of 2p orbitals with *B* symmetry.<sup>2</sup> It follows that the wave function of the unpaired spin must be that of a nonbonding  $2p_y$  orbital.

The creation of the hole results in a substantial elongation of the Si-O distances, from  $1.62\pm0.01$  to  $1.81\pm0.02$  Å, Table I. The elongation,  $\approx 0.2$  Å, is even larger than that obtained by Edwards using a similar approach.<sup>7</sup> The distance of the Si atoms from the next-nearest-neighbor O atoms, on the other hand, decreases by  $\approx 0.03$  Å, in the ionized system. A very similar effect is found when one Si atom is replaced by Ge. Also, in this case in fact we are able to obtain a solution where the hole is completely localized, Table IV. The Si-O and the Ge-O distances increase by about 0.16 Å, Table III; the other Si-O and Ge-O distances in the cluster decrease by a small amount. This latter effect, however, is partially the consequence of the constrained imposed by the fixed H atoms at the cluster border. In reality, the expansion due to the hole formation will extend beyond the second shell of O neighbors. Therefore, the calculations show a substantial relaxation of the lattice around the ionized O atom in a STH<sub>1</sub> center, supporting the idea of a small polaron associated with this kind of defect.

The hole localization results in an O atom in the lattice with different charge from the rest. The real charge distribution in the cluster can be deduced from the analysis of the Mulliken population, but also from the changes in the O 1*s* core level binding energies (CLBE's). CLBE's, in fact, are

TABLE IV. Spin distribution in STH<sub>1</sub> and STH<sub>2</sub> models.<sup>a</sup>

System		Cluster and symmetry	Spin density <sup>b</sup>
STH <sub>1</sub>	$\equiv$ Si $-0^+$ $-$ Si $\equiv$	$A, C_1$	1.04(O <sub>1</sub> )
		$B, C_1$	$1.02(O_1)$
STH <sub>1</sub> (Ge)	$\equiv$ Si $-0^+$ $-$ Ge $\equiv$	$A, C_1$	$1.02(O_1)$
$STH_2$	(-O-Si-O-) <sup>+</sup>	$B, C_1$	0.57(O <sub>2</sub> )
			0.57(O <sub>3</sub> )

<sup>a</sup>AE UHF results.

<sup>b</sup>See Fig. 1 for a definition of the atoms where the spin is localized.

very sensitive to a change in the electron density in the valence. The data of Table V show that the number of electrons associated with the bridging oxygen atom decreases from  $\approx 8.8$  in the neutral model of  $\alpha$ -quartz to  $\approx 8.4$  in STH<sub>1</sub>, Table V;  $\Delta q$  is therefore of +0.4 electrons and not of +1 electron as one would expect. A proof of the charge localization on the bridging oxygen atom comes from the inspection of the CLBE's and of their shifts,  $\Delta BE$ , as one goes from the neutral to the ionized system. The CLBE's have been obtained based on Koopmans' theorem as  $-\varepsilon_i$ , where  $\varepsilon_i$  is the corresponding one-electron eigenvalue.<sup>27</sup> This approach neglects final-state relaxation effects and gives only qualitative estimates of the BE shifts. The presence of a positive charge on the system leads to a strong and uniform stabilization of the core levels of all atoms, by about 5-5.5 eV, but a much more pronounced shift,  $\approx 9$  eV, is found in correspondence of the bridging O1 atom. This result clearly indicates the localization of the hole on the O atom, with a corresponding increase of the effective nuclear potential and shift of the corresponding core levels to higher binding energies.

The cluster *B*, Fig. 1(c), has been employed to model a  $STH_2$  center. Two variants of this cluster have been considered, one with imposed  $C_2$  symmetry and one without any symmetry element  $C_1$ . In this latter case the hole can localize at any O atom of the cluster, leading to another model of  $STH_1$ ; in the first case, the hole is forced to be delocalized over two equivalent O atoms, either  $O_1$  and  $O_2$  or  $O_3$  and  $O_4$ , Fig. 1(c). This requires that the dihedral angles at the site are such to have the  $2p_y$  nonbonding orbitals of *B* type pointing

TABLE V. Charge differences  $\Delta q$  and core level binding energy shifts  $\Delta BE$ , in STH<sub>1</sub> with respect to the regular lattice.<sup>a</sup>

$\Delta$ (neutral-charged)	$\equiv$ Si $-0^+$ $-$ Si $\equiv$	$\equiv$ Si $-0^+$ $-Ge\equiv$
$\Delta q(O_1)$	+0.39	+0.43
$\Delta q(\mathrm{O}_{2-7})$	+0.06	+0.05
$\Delta q(Si)$	-0.04	-0.04
$\Delta q$ (Ge)		-0.02
$\Delta BE (O_1 \ 1s) (eV)$	-8.6	-9.1
$\Delta BE (O_{2-7} \ 1s) (eV)$	-5.0	-5.1
$\Delta \text{BE}$ (Si 2p)	-5.0	-5.5
$\Delta BE (Ge 3p)$		-5.5

<sup>a</sup>Charges from Mulliken population, binding energies, BE, from Koopmans' theorem.

at each other. Starting with the  $C_2$  model, we found indeed that the hole is uniformly distributed over O<sub>1</sub> and O<sub>2</sub>, Table IV. The charge density obtained from this calculation was then used as a starting point of the calculation in  $C_1$  symmetry, and in the final UHF SCF solution the hole remains delocalized. Notice that in the  $C_1$  model the two O atoms are no longer equivalent. In order to make sure that this result is not an artifact due to the use of a symmetric density as a starting point, we repeated the calculation by inducing a moderate distortion in the initial geometry, but we obtain a very similar spin distribution as in the previous calculation. This indicates that the delocalized hole, which for the moment we tentatively identify with the STH<sub>2</sub> center proposed by Griscom,<sup>5</sup> is possibly a local minimum. However, we cannot exclude that the energy surface is very flat and that the SCF wave function can evolve in a complete hole localization. Indeed, when the calculations with cluster B were repeated in  $C_1$  symmetry by using as a starting point the density of the neutral system, the ionization results in a complete localization of the hole on one of the four O atoms of the cluster; see Table IV (the results are practically independent of the atom where the localization occurs). The system models therefore a STH<sub>1</sub> center, and the geometrical relaxation is practically identical to that found with the smaller cluster A. The fact that two different solutions have been determined with the same cluster, corresponding to  $STH_1$ and STH<sub>2</sub>, allows us to compare the relative stability of the two centers. The total energy of  $STH_1$  is 1.8 eV lower than that of  $STH_2$ . Thus, while  $STH_2$  can exist as a metastable center, its energy is definitely higher than that of a STH<sub>1</sub>.

The full geometry optimization of the STH<sub>2</sub> center, the delocalized hole, shows a much smaller geometrical relaxation than in STH<sub>1</sub>, Fig. 1(c) and Table II. The Si-O distances involving the O atoms where the hole is formed, in fact, show an elongation with respect to the neutral system of about  $0.04 \pm 0.01$  Å, i.e., 4 times smaller than in STH<sub>1</sub>. On the other hand, a non-negligible change occurs in the O-Si-O angle which decreases from values typical of tetrahedral coordination to 84°, Table II. In a sense, by allowing the O-Si-O angle to close down considerably we were able to find a STH<sub>2</sub>-type trap, making the defect a molecular polaron. In this respect, the model is different from that proposed by Griscom where the hole is not delocalized, but hops between two oxygens very rapidly.<sup>5</sup> Furthermore, it is hard to accept that the structure of  $\alpha$ -quartz will undergo the large geometrical distortion predicted by the calculations; indeed, no evidence has been reported of STH<sub>2</sub> in quartz. In the Griscom model for the amorphous material the hole could be trapped over two oxygen atoms without the formation of a molecular polaron (a special case of Anderson localization) thanks to the presence of special dihedral angles in the network. Therefore, our model of a delocalized hole can be simply viewed as an average structure between two rapidly interchanging states where the hole hops from  $O_1$  to  $O_2$ . The computed electronic properties of this average structure provide a basis for a comparison with the experimental measures.

To summarize this section, we have seen that  $STH_1$  and  $STH_2$  centers have different characteristics, being localized and delocalized, respectively. Both exhibit a large geometrical relaxation. The adiabatic ionization potential, computed

at the HF level, is of 9.48 eV for STH<sub>1</sub> and 9.15 eV for STH<sub>2</sub>, respectively; the vertical ionization potentials (IP's) are even higher,  $\approx 11.3$  eV. When in its minimum geometry, the STH<sub>2</sub> center is structurally different from that identified by Griscom<sup>5</sup> (hopping hole) and can be classified as a molecular polaron. In the next section we analyze the ESR properties, in particular the hfcc's, of these two centers.

#### **B.** Hyperfine interactions

ESR spectra and computer line shape simulations have shown two distinct types of STH's; two sets of g values have been identified.<sup>5</sup> Isotopically enriched samples have been used to determine the hfcc's of the unpaired electron with the <sup>17</sup>O and <sup>29</sup>Si nuclides. In particular, the <sup>29</sup>Si hyperfine structures have led to the suggestion that the unpaired spin of  $STH_1$  is confined to a pure 2p nonbonding orbital of a single bridging oxygen, while the hole of STH<sub>2</sub> is rapidly tunneling between a pair of nonbonding O 2p orbitals belonging to two adjacent bridging oxygen atoms.<sup>5</sup> No attempt to optimize the <sup>29</sup>Si hfcc's has been done in Ref. 5; however, hfcc's of 0.8 mT have been measured by Hayes and Jenkin in a Ge-doped silica sample.<sup>2</sup> Hyperfine interactions with <sup>73</sup>Ge could not be detected;<sup>2</sup> still, we report our computed values in Table VI. The value of the hfcc's with  $^{29}$ Si in STH<sub>1</sub>, 0.8 mT, implies that the overlap of the wave function of the unpaired spin with a Si nucleus is small and indicates a substantial localization of the hole on the O atom(s). Similar or smaller values of the <sup>29</sup>Si hfcc have been used by Griscom in a computer simulation of the STH<sub>2</sub> spectrum.<sup>5</sup> The measured <sup>17</sup>O hfcc's are  $A_1 \approx 11 \text{ mT}$ ,  $A_2 \approx A_3 \approx 1.6 \text{ mT}$  for STH<sub>1</sub> and  $A_1 \approx 6.2 \text{ mT}, A_2 \approx A_3 \approx 1.3 \text{ mT}$  for STH<sub>2</sub>.<sup>5</sup>

The computed hfcc's with <sup>29</sup>Si, <sup>73</sup>Ge, and <sup>17</sup>O are reported in Tables VI and VII, respectively. Where a comparison with the experiment is possible, the agreement is good. The <sup>29</sup>Si hfcc's are essentially isotropic and are very close to those reported by Hayes and Jenkin;<sup>2</sup> the small values are consistent with the strong localization of the unpaired spin on the bridging O atom in STH<sub>1</sub>. The calculations show a small difference,  $\approx 0.1$  mT, in the hfcc's of the two Si atoms nearest to the ionized O; this small difference reflects the slightly different Si-O distances in  $\alpha$ -quartz, but is probably undetectable in amorphous silica.

For the model of STH<sub>2</sub> we performed two calculations. According to the model proposed by Griscom,<sup>5</sup> the hopping process is faster than the Larmor frequency ( $\approx 10^8 \text{ s}^{-1}$ ); this implies that the STH<sub>2</sub> site does not relax and the geometry remains close to that of the glass before hole trapping. We have modeled this situation by computing the hfcc's for the unrelaxed structure of cluster B, i.e., for the structure of the neutral lattice; see "STH2 unrelaxed" in Table VI. The other possibility is that the hole becomes effectively delocalized over two O atoms and that a geometrical relaxation accompanies the hole formation (molecular polaron). This is described by the hfcc's of the fully relaxed structure; see "STH<sub>2</sub> relaxed" in Table VI. In the unrelaxed structure the hfcc of Si<sub>1</sub> $\approx$ 2 mT is similar to that of the adjacent Si<sub>2</sub> and Si<sub>3</sub> atoms, Table VI. In the relaxed model Si2 and Si3 have much smaller values,  $\approx 0.7$  mT. This difference can be understood in terms of the geometrical change accompanying the hole formation. In relaxed STH<sub>2</sub> the Si<sub>1</sub>-O<sub>1</sub> distance, 1.657 Å, is

Atoms<sup>b</sup>  $A_3$ Center  $B_1$  $B_2$  $B_3$  $a_{iso}$  $A_1$  $A_2$ +0.750.00 +0.74+0.75 $Si_1$ -0.01+0.01+0.76STH<sub>1</sub> Theory +0.95-0.020.00 +0.02+0.93+0.95+0.97 $Si_2$ Ge +0.52-0.010.00 +0.52+0.53+0.01+0.51STH<sub>1</sub> (Ge) Theory -0.04Si +1.05-0.01+0.05+1.01+1.04+1.10 $STH_1$ Expt. (Ref. 2) Si 0.8 0.8 0.8  $Si_1$ +2.01-0.09-0.09+0.18+1.92+1.92+2.19STH<sub>2</sub> unrelaxed Theory Si2,Si3 +2.34-0.10-0.04+0.13+2.24+2.30+2.38 $Si_1$ +2.21-0.10-0.06+0.16+2.11+2.15+2.37STH<sub>2</sub> relaxed Theory Si2,Si3 +0.78-0.060.00 +0.06+0.72+0.78+0.84 $Si_1$ 1.0 1.0 1.0 STH<sub>2</sub> Expt. (Ref. 5)<sup>c</sup> 0.5 0.4 0.5 Si<sub>2</sub>,Si<sub>3</sub>

TABLE VI. <sup>29</sup>Si and <sup>73</sup>Ge hyperfine coupling constants, in mT, of STH<sub>1</sub> and STH<sub>2</sub> centers in pure and Ge-doped α-quartz.<sup>a</sup>

<sup>a</sup>Results from clusters A and B at the AE level and  $C_1$  symmetry.

<sup>b</sup>See Fig. 1.

<sup>c</sup>hfcc's used in computer simulations.

about 0.1 Å shorter than the  $Si_2$ -O<sub>1</sub> one, Table II, and the Fermi contact term with  $Si_2$  and  $Si_3$  is smaller. The <sup>29</sup>Si hfcc values determined for the STH<sub>2</sub> models are similar to those assumed by Griscom in the computer simulation of the ESR spectrum,<sup>5</sup> Table VI. However, the values computed for the relaxed structure are closer to the experimental ones; in particular, the larger value for the central Si compared to the neighboring Si atoms is correctly reproduced. The absolute difference, however, is rather small, and the present results about the nature of STH<sub>2</sub>, relaxed or unrelaxed, are not conclusive.

Various approaches have been used to study the <sup>17</sup>O hfcc's (AE, ECP, different basis sets, etc.), but the results show a considerable stability as a function of the details of the computation, Table VII. The  $A_1$  values are slightly over-

estimated, by  $\approx 2-3$  mT, with respect to the experimental ones,<sup>5</sup> while the  $A_2$  and  $A_3$  values are somewhat lower than in the experiment. However, the general features are correctly reproduced. In particular, the principal component of the hfcc's for STH<sub>2</sub> is about 60% of that of STH<sub>1</sub>. Notice that the hfcc's of <sup>17</sup>O for the unrelaxed and relaxed forms of STH<sub>2</sub> are similar, Table VII; both  $a_{iso}$  and the *B* tensor values are larger for the relaxed structure, consistent with a more pronounced localization of the hole on the bridging oxygens.

The present results for  $STH_1$  are similar to those obtained by Edwards<sup>7</sup> for the same center and substantially disagree with the semiempirical calculations of Chernov *et al.*<sup>4</sup> who obtained a complete delocalization of the hole on the O atoms of the cluster. The results for  $STH_2$  are sufficiently close

Method	Cluster and symmetry	$a_{\rm iso}$	$B_1$	$B_2$	<i>B</i> <sub>3</sub>	$A_1$	$A_2$	$A_3$
		S	ГН <sub>1</sub> , <u></u> Si–	-O <sup>+</sup> -Si	_			
AE	$A, C_1$	-4.78	-9.07	4.51	4.56	-13.85	-0.27	-0.22
ECP	$A, C_2$	-5.14	-8.98	4.47	4.51	-14.12	-0.63	-0.67
AE	$B, C_1$	-4.76	-8.92	4.39	4.54	-13.68	-0.37	-0.22
Expt. Ref. 5						11.4	$\approx 1.7$	≈1.7
		STH	$_1$ (Ge), $\equiv S$	i—O <sup>+</sup> —0	Ge≡			
AE	$A, C_1$	-4.80	-8.97	4.47	4.50	-13.77	-0.33	-0.30
ECP	$A, C_1$	-5.04	-8.95	4.43	4.52	-13.99	-0.61	-0.52
			STH <sub>2</sub> (-O-	Si-O-)+				
AE	$B, C_1$	-3.13	-4.85	2.41	2.44	-7.98	-0.72	-0.69
	Unrelaxed							
AE	$B, C_1$	-3.90	-5.86	2.92	2.93	-9.75	-0.97	-0.96
	Relaxed							
Expt. Ref. 5						6.2	≈1.3	≈1.3

TABLE VII. <sup>17</sup>O hyperfine coupling constants, in mT, of STH<sub>1</sub> and STH<sub>2</sub> in pure and Ge-doped  $\alpha$ -quartz.

System	State	Character	nM/nR	$\Sigma_i c_i^2$	$T_e ({ m eV})$	f(r)
STH <sub>1</sub>	$X 1 {}^{2}A$	$2p_{y}(O_{1})^{1}$	22 <i>M</i> /4 <i>R</i>	0.95	0.0	
	$2^{2}A$	$2p_z(O_1)^2 \rightarrow 2p_y(O_1)^1$	22M/4R	0.95	0.50	$6 \times 10^{-6}$
	$3^{2}A$	$2p_x(O_1)^2 \rightarrow 2p_y(O_1)^1$	22M/4R	0.95	2.70	$2.5 \times 10^{-3}$
	$4^{2}A$	$2p(O_{2-7})^2 \rightarrow 2p_y(O_1)^1$	22M/4R	0.94	3.53	0.012
STH <sub>1</sub> (Ge)	$X \ 1^{-2}A$	$2p_{v}(O_{1})^{1}$	23M/4R	0.94	0.0	
	$2^{2}A$	$2p_z(O_1)^2 \rightarrow 2p_v(O_1)^1$	23M/4R	0.94	2.64	$6 \times 10^{-5}$
	$3^{2}A$	$2p_x(O_1)^2 \rightarrow 2p_y(O_1)^1$	23M/4R	0.95	2.53	$3.4 \times 10^{-4}$
	$4^{2}A$	$2p(O_{2-7})^2 \rightarrow 2p_y(O_1)^1$	23M/4R	0.93	3.20	0.022

TABLE VIII. Optical transitions of a STH<sub>1</sub> center in pure and Ge-doped  $\alpha$ -quartz.

<sup>a</sup>Twenty-one frozen core orbitals, 25 virtual orbitals discarded, total active space 57 orbitals, and 27 electrons. The number of generated configurations is larger than  $10^7$ , and the selected configurations are  $\approx 5000$ .

to the experimental data obtained by Griscom to support his assignment of a  $STH_2$  center to a hole hopping over two neighboring O atoms.<sup>5</sup>

## C. Optical transitions and analysis of g values of $STH_1$

Photobleaching of STH centers by photons of 1.5-2.5 eV has been observed,<sup>28</sup> indicating that optical absorption of STH's should exist in this range of energies. Indeed, Jenkin *et al.*<sup>6</sup> and Chernov *et al.*<sup>4</sup> have reported the existence of a band around 550 nm (2.25 eV) in both pure and Ge-doped silica and assigned this feature to a STH center. Jenkin *et al.*<sup>6</sup> observed also a second band at 4.2 eV and attributed this band to a Ge<sup>3+</sup> center. The band at 2.24 eV has also been observed by Mori *et al.* in silica glass.<sup>29</sup>

An indirect measure of the transition energies in STH<sub>1</sub> can be obtained from the theory of *g* values. We assume the same notation used by Griscom,<sup>5</sup> so that if the unpaired electron in the ground state of STH<sub>1</sub> lies in a pure O  $2p_z$  orbital (this corresponds to the  $2p_y$  orbital in our previous notation), the first excited state is of almost pure O  $2p_x$  character. According to Griscom,<sup>5</sup> the following excitation corresponds to a hole in a Si-O-Si bonding state with partial O  $2p_y$  character. The *g* values can then be expressed in terms of the relative position of the ground and excited states as

$$g_{zz} \approx g_e, \qquad (4)$$

$$g_{yy} \approx g_e + 2\lambda/\Delta,$$
 (5)

$$g_{xx} \approx g_e + 2\lambda/E, \tag{6}$$

where  $\lambda$  is the spin-orbit coupling constant for oxygen,  $\Delta = E_0 - E_1$  is the first 2p - 2p transition energy, and  $E = E_0 - E_2$  is the second 2p - 2p transition. Taking a commonly accepted value for  $\lambda$  from O<sup>-</sup>, 0.014 eV,<sup>30,31</sup> and using the experimentally measured values of  $g_1 = g_{zz} = 2.0027$ ,  $g_2 = g_{xx} = 2.0082$ , and  $g_3 = g_{yy} = 2.043$ , Griscom<sup>5</sup> obtained for the two lowest excitations 0.67 and 4.75 eV, respectively. If, on the other hand, one uses the experimental values of  $\lambda$  for O and O<sup>-</sup> reported by Zeller and Känzig,<sup>32</sup> 0.0186 and 0.0236 eV, respectively, the transition energies estimated from ESR become 0.91 and 6.3 eV ( $\lambda = 0.0186 \text{ eV}$ ) or 1.16 and 8.0 eV ( $\lambda = 0.0236 \text{ eV}$ ). No matter which value of  $\lambda$  is taken, the transition at 2.25 eV is not predicted. A possible interpretation is that the relations (4)–(6), based on perturba-

tion theory, only account for the local 2p-to-2p transitions within the same O atom and not for other more delocalized transitions. If this is true, one has to assume that the origin of this band is different. Skuja proposed<sup>33</sup> that the optical band around 2 eV due to a nonbridging oxygen hole center NBOHC  $\equiv$ Si-O<sup>•</sup>, is due to the excitation from three neighboring oxygens. Our recent calculations on this center fully agree with this assignment.<sup>12</sup> It is possible that a similar mechanism works for a STH<sub>1</sub> center.

Following our previous work on the ab initio computation of optical transitions of point defects in silica,<sup>11-14</sup> we have determined the energies and oscillator strengths of the transitions associated with the previously described model of STH<sub>1</sub> in pure and Ge-doped silica. Previous experience has shown that the transition energies of point defects in silica can be predicted with typical errors of a few tenths of an eV, at least for neutral defects.<sup>11–14,16</sup> Here the situation is considerably more complex for at least two reasons. The first one is that we are dealing with a charged system, and longrange polarization effects in the ground and excited states can be different and not properly included in a small cluster model. The second one is related to the hole localization and to orbitals used to generate the CI space, as will be discussed below. For these reasons we do not expect for this system the same level of accuracy obtained in our previous studies.

The optical transitions of  $STH_1$  have been determined by means of MRDCI calculations, Table VIII. To reduce the size of the CI expansion, an ECP has been used on both Si and Ge atoms, but this does not affect the transition energies by more than 0.1 eV.<sup>16</sup> In general, MRDCI wave functions provide a very good description of ground and exited states, but to obtain reliable energy differences it is necessary to use a similar zero-order, or reference space, description of the states involved. In this respect the calculation of the optical transitions in STH<sub>1</sub> poses some technical problems. In fact, as we have shown above, the hole is fully localized on a nonbonding 2p orbital of the central oxygen. This results in a large splitting of the 2p levels of the O atom. Starting the CI calculation from a set of SCF orbitals for the cation leads to a solution which is biased by the strong splitting of the 2plevels. Therefore, we decided to adopt the following strategy. We used the optimal geometry of a STH<sub>1</sub> (see Table I or III), but we computed a RHF wave function for the neutral closed-shell state. In this way the nonbonding O 2p orbitals of the central atom are at similar energies. We used these orbitals to perform the CI calculation for the ionized state,  $STH_1$ . Exactly the same procedure has been followed for the Ge-doped variant of  $STH_1$ . The computational approach adopted represents a way to obtain a more balanced description of the various excited states at the expense of larger error bars in the transition energies.

We consider first the model of STH<sub>1</sub> in pure silica. We searched for the three lowest roots in the CI secular problem. The first excited state corresponds to the excitation from a doubly occupied nonbonding 2p level on the bridging oxygen to the singly occupied 2p orbital. This state is 0.50 eV above the ground state, but has virtually no intensity, Table VIII. The existence of a low-lying 2p-to-2p transition is in agreement with the analysis of the g values.<sup>5</sup> The next excited state is also a local transition and involves the third 2plevel on the bridging O atom with bonding character with the Si neighbors. This excitation is found at 2.70 eV and has an oscillator strength  $f \approx 10^{-3}$ . According to the analysis of the g values, the second 2p-to-2p excitation should occur at much higher energy, 4.5 eV.<sup>5</sup> It should be mentioned, however, that the computed  $T_e$ 's must be considered with great care. In fact, if one uses for the same transitions SCF orbitals optimized on the ionic ground state, the first excitation occurs at 1.6 eV, while the second 2p-to-2p excited state is found around 5 eV. Clearly, these differences are very large and cast some doubts on the reliability of the absolute values of the  $T_e$ 's. Using the set of orbitals from the neutral state, we found another transition at 3.53 eV which has a different character, Table VIII. This excitation in fact involves the external O atoms of the cluster; it can be described as an excitation from the 2p nonbonding levels of the nearest O atoms to the central one. Notice that the intensity of this excitation is higher than for previous cases. Very little changes are found on the  $T_e$ 's when Si is replaced by Ge: the three lowest excitations are found at 0.64, 2.53, and 3.20 eV, respectively, above the ground state and have the same character and similar intensities as in pure silica.

These results could suggest a tentative assignment of the 2p-to-2p transitions computed at 2.5–2.7 eV to the observed band at 2.25 eV.<sup>2</sup> However, it is more likely that the transition computed at 3.2–3.5 eV in our models (excitation from the neighboring O atoms to the central one) is the real origin of the band at 2.25 eV. There are two arguments in favor of this possibility. First of all, the neighboring O atoms have been treated with a less flexible basis set than the central one (no *d* polarization functions have been included). A better description of these atoms will reduce the excitation energy. Furthermore, this kind of transition has been proposed to explain the band at about 2 eV due to NBO centers in silica.<sup>33</sup> Recent calculations based on the same approach used here fully support this view.<sup>12</sup>

## **IV. CONCLUSIONS**

The electronic structure and spectral properties of two variants of self-trapped holes in silica have been investigated by means of cluster models and *ab initio* wave functions. Clusters of different sizes have been employed to describe the STH<sub>1</sub> center, consisting of a hole trapped at a 2p non-bonding orbital of an O atom bridging two Si atoms, and the STH<sub>2</sub> center, a metastable defect where the hole is rapidly

tunneling between two bridging O atoms. This latter situation has been modeled by a hole delocalized over two bridging O atoms. The two centers exhibit characteristic spectral features in ESR: in particular, the hyperfine coupling constants with the <sup>17</sup>O and <sup>29</sup>Si nuclides provide a fingerprint of their different nature. The analysis is not restricted to a model of pure silica, but also to Ge-doped silica. In this respect, no significant difference is found in the <sup>17</sup>O and <sup>29</sup>Si hfcc's of the Ge-containing STH<sub>1</sub> center: this can be considered as a strong proof of the extremely localized nature of the defect. In both pure and Ge-doped silica, STH<sub>1</sub> is characterized by a strong elongation of the Si-O distances. This justifies the classification of this center as a small polaron as proposed by Jenkin *et al.*<sup>6</sup> When the structure of  $STH_2$  is geometrically optimized, one observes a small elongation of the Si-O bonds compared to the regular lattice, but also a significant reduction of the O-Si-O angle, from the classical tetrahedral value of  $\approx 109^{\circ}$  to about 85°. This is different from what suggested by Griscom, who found no distortion of this angle.<sup>5</sup> The hyperfine coupling constants for two models of STH<sub>2</sub>, with and without geometrical relaxation, are quite similar, although the relaxed model is in slightly better agreement with the experiment. It should be mentioned that in STH<sub>2</sub> the hole tunnels between two adjacent sites on a time scale shorter compared with the time required for the lattice to respond. Indeed, Griscom suggested that STH<sub>2</sub> is an example of an Anderson localized hole with rapid tunneling between nearly degenerate 2p state on neighboring oxygens.5

Finally, we performed configuration interaction calculations on the lowest electronic transitions of a STH<sub>1</sub> center in pure and Ge-doped silica. In both cases we found the lowest excited state, corresponding to a local  $O(2p) \rightarrow O(2p)$  transition, at about 0.5–0.6 eV above the ground state; the corresponding intensity is almost zero. The second transition occurs at higher energy, 2.5-2.7 eV, and involves the excitation of one electron from the third O 2p level with bonding character with the Si atoms to the singly occupied O 2porbital. Also, this transition has a low intensity. We found a third exited state at somewhat higher energy, about 3.2-3.5 eV. This latter state corresponds to an excitation from the nonbonding 2p levels of the neighboring O atoms to the O atom where the hole is localized. This transition has a larger intensity. The results of the calculations are not sufficient to attempt a direct assignment. However, combining the theoretical results with the data obtained from the analysis of the g values it is possible to conclude that (a) three excited states are present for a STH<sub>1</sub> center, but only one with appreciable intensity, and (b) the band observed at 2.25 eV is likely due to the excitation from the neighboring oxygens, in full analogy with what is found for a nonbridging oxygen hole center.33

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