PHYSICAL REVIEW B VOLUME 56, NUMBER 12 15 SEPTEMBER 1997-II

Ab initio formation energies of point defects in pure and Ge-doped SiO_2

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(Received 27 December 1996; revised manuscript received 28 May 1997)

We have studied by means of *ab initio* calculations including electron correlation and cluster models the formation energies of a series of defects in bulk SiO_2 and in silica glasses containing Ge impurities. The defects considered include oxygen vacancies, ≡Si—Si≡, peroxyl linkages, ≡Si—O—Si≡, peroxyl radicals, ≡Si—O—O$^{\bullet}$, other radicals, ≡Si—O$^{\bullet}$ and ≡Si$^{\bullet}$, E' centers, ≡Si$^{\bullet}$ $^{+}$Si≡, double oxygen vacancies, ≡Si—Si—Si≡, Frenkel pairs, ≡Si—Si—O—O—Si≡, etc. The corresponding analogs with Ge atoms replacing the network Si atoms have also been considered. We found that the formation of a single oxygen vacancy, defined as the energy required to remove and bring to infinity a neutral O atom, is 8.5 eV. This is consistent with the most recent thermodynamic estimates. The stability as well as the geometry of the other defects is discussed. It is shown that in the presence of Ge impurities the formation of oxygen deficient centers occurs at a lower energy cost. [S0163-1829(97)04835-2]

I. INTRODUCTION

Structural defects in crystalline and amorphous silica are of great technological importance for the properties of optical fibers.[1] A considerable number of experimental studies has been dedicated to the optical response of oxygen deficient centers or of other defects in pure and Ge-doped silica glasses.[2–11] The presence of these centers is accompanied by typical absorption and luminescence spectra[1–11] due to characteristic impurity states in the band gap.[12] Despite the substantial experimental effort in the characterization of these defects, also by means of other spectroscopies, in particular electron paramagnetic resonance[7] many of the assignments remain tentative. It is only recently that calculations of the absorption energies and intensities of these defects have been reported at a sufficiently high level of accuracy to provide a firm assignment.[13]

While the experimental data on the optical transitions of silica defects are abundant, although not fully understood, almost nothing is known on the thermodynamics of the defects formation. Calorimetric experiments have been performed to provide estimates of the formation energies of dominant defects in nonstoichiometric oxides,[14] but to the best of our knowledge no experimental data are available for the formation energy of an oxygen or silicon vacancy in α-quartz or amorphous silica. The only estimates reported so far are based on theoretical calculations but the values differ significantly depending on the computational approach used.[15–18] The simplest, but also most important defect in SiO_2 is the oxygen vacancy corresponding to the process ≡Si—O—Si≡→≡Si—Si≡+O; two Si—O bonds are broken and replaced by a single Si—Si bond. Early estimates based on extended Hückel calculations and cluster models gave about 10 eV for the energy associated to this process in α-quartz.[15] Even higher values have been obtained by more recent semiempirical quantum-mechanical studies on amorphous silica.[16] The first *ab initio* estimate has been reported in 1990 based on local-density functional (LDF) band-structure calculations.[17] It was found that the creation energy in α-quartz is 7.9 eV (Ref. 17) but it is well known that the LDF approach considerably overestimates the binding energies. Indeed, using a formally exact embedding scheme of the defect in the host crystal, a much smaller formation energy, about 5 eV, was obtained by means of *ab initio* Hartree-Fock calculations.[18] In the same work a value of about 6 eV was found based on the semiempirical modified neglect of differential overlays approach and a $Si_8O_7H_{18}$ cluster.[18] Very recently, it has been observed that the *ab initio* Hartree-Fock estimate of 5 eV is not consistent with thermodynamic criteria.[19] In fact, the analysis of the experimental enthalpies of formation suggests that a reasonable lower bound for the formation energy of an oxygen vacancy in SiO_2 is 7.3 eV.[19] Thus, not only the data are scarce, but also not fully consistent.

In this paper, we report a systematic investigation of the formation energies for a series of defects in pure and Ge-doped silica. These include oxygen vacancies, ≡Si—Si≡, peroxyl linkages, ≡Si—O—O—Si≡, peroxyl radicals, ≡Si—O—O$^{\bullet}$, other radicals, ≡Si—O$^{\bullet}$ and ≡Si$^{\bullet}$, E' centers, ≡Si$^{\bullet}$ $^{+}$Si≡, double oxygen vacancies, ≡Si—Si—Si≡, Frenkel pairs, ≡Si—Si—O—O—Si≡, etc. The corresponding analogs with a Ge substitutional impurity have also been studied. Finally, we also considered the formation energy of a Si vacancy. The calculations are based on cluster models and correlated wave functions. We will show that the computational approach gives reliable estimates of the formation energies provided that the basis sets used for the construction of the wave functions are sufficiently flexible and that correlation effects are properly taken into account. The computation of a series of defects treated at the same level of accuracy allows one to derive important information about the absolute and relative thermodynamic stability of a given defect. The comparison between pure and Ge-doped SiO_2 is important for the understanding of the properties of these materials.

The paper has been organized as follows. In Sec. II we describe the computational method used. In Sec. III we give a brief discussion of the geometrical parameters of the defects considered (in particular bond lengths and bond angles). Section IV is dedicated to the formation energies.

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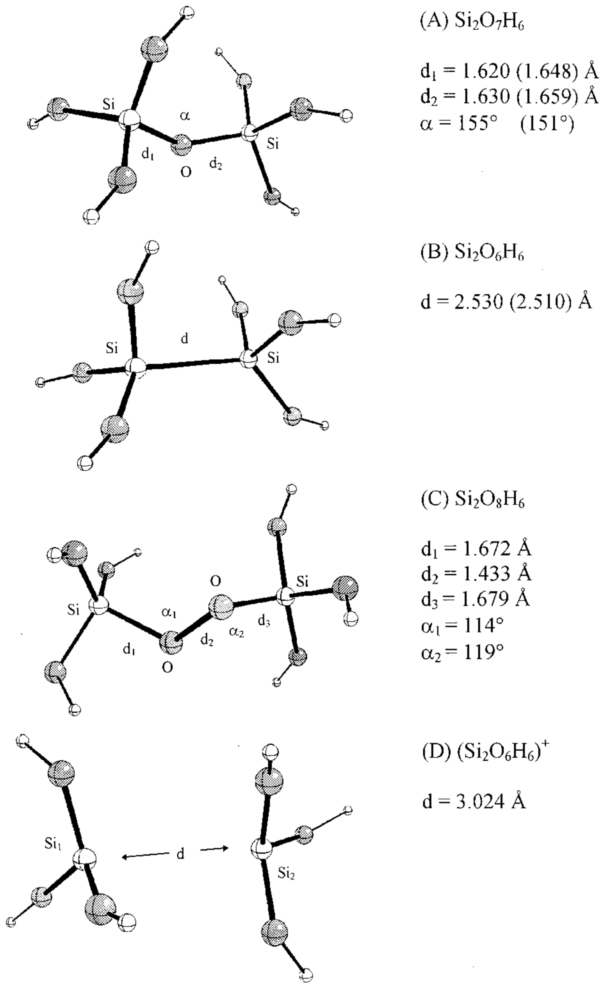

FIG. 1. $Si_2O_xO_6$ cluster models of local defects in α-quartz. (A) Regular crystal. (B) Single oxygen vacancy. (C) Peroxyl group. (D) E' center. Geometrical parameters computed at the HF/HF(d) level (see text). Results at the MP2/MP2(d) level are in parentheses.

We first discuss the validity of our approach, the effect of basis sets, cluster size, and electron correlation (Sec. IV A). Section IV B is devoted to the defects in pure SiO_2, while the same defects involving a Ge substitutional impurity are discussed in Sec. IV C. In Sec. IV D we briefly discuss the formation energy of a Si vacancy. The conclusions are summarized in the last section.

II. COMPUTATIONAL DETAILS

A. Cluster models and wave functions

The calculations have been performed within the cluster model approach, a technique which is particularly appropriate to study localized phenomena, like defects and impurity states.[20] Clusters of various size have been used to model regular and defect sites in the bulk of α-quartz. The cluster dangling bonds have been saturated by H atoms, a commonly used technique to ''embed'' clusters of semiconducting or insulating materials.[21–31] The positions of the cluster atoms were initially fixed to those of α-quartz derived from x-ray diffraction data at 94 K.[32] The embedding H atoms were fixed at a distance of 0.96 Å from the respective O atoms along the O—Si directions of α-quartz. The position of all the Si and O atoms of the cluster has been fully optimized. The fixed H atoms provide a simple representation of the mechanical embedding of the solid matrix.

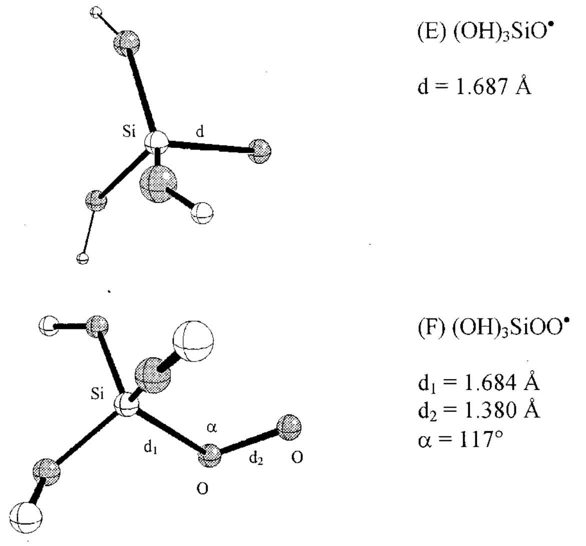

FIG. 2. SiO_xH_3 cluster models of local defects in α-quartz. (E) ≡Si—O$^•$ radical. (F) ≡Si—OO$^•$ peroxyl radical. Geometrical parameters computed at the HF/HF(d) level (see text).

All electron Hartree-Fock (HF) self-consistent field wave functions have been constructed using double-zeta (DZ) Gaussian-type orbital basis sets on Si and O atoms.[33] One d-polarization function of exponent $\alpha=0.4$ has been added to the Si basis set. The final value of the formation energy has been computed by adding a d-polarization function ($\alpha=0.74$) to the basis set of the O atoms directly involved in bond breaking. The final basis sets are $[12s8p1d/6s4p1d]$ (Si) and $[10s5p1d/3s2p1d]$ (O). Comparison of results with and without d functions shows that they are essential for a proper description of the formation energies but not for the determination of the optimal geometries (see below). A DZ $[4s/2s]$ basis set was used for the H atoms.[33] For the models of Ge-doped silica we employed an effective core potential for Ge which includes in the core the $1s^2$ to $3p^6$ electrons and treats explicitly only the $4s^2$ and $4p^2$ valence electrons.[34] The basis set for the Ge atoms is $[3s3p/2s2p]$. Also in this case we added a d-polarization function of exponent $\alpha=0.246$. The radical states have been computed according to the restricted open Hartree-Fock (ROHF) formalism. Inclusion of electron correlation at MP2 level (see below) for open shell states required the determination of unrestricted HF (UHF) wave functions. The values of $\langle S^2\rangle$ for UHF wave functions show pure doublet states with virtually no spin contamination.

Geometry optimizations have been performed at the HF, ROHF, and MP2 levels by computing analytical gradients of the total energy. Given the low local symmetry of the crystal, all the clusters are computed without any symmetry element (C_1 symmetry group). The clusters used are $Si_2O_7H_6$, $Si_3O_{10}H_8$, and $Si_5O_{16}H_{12}$ for the nondefective structures, see Figs. 1–4. The models of an oxygen vacancy, $Si_2O_6H_6$, Fig. 1, and of a double oxygen vacancy, $Si_3O_8H_8$, Fig. 3, have been obtained by removing one (or two) oxygen

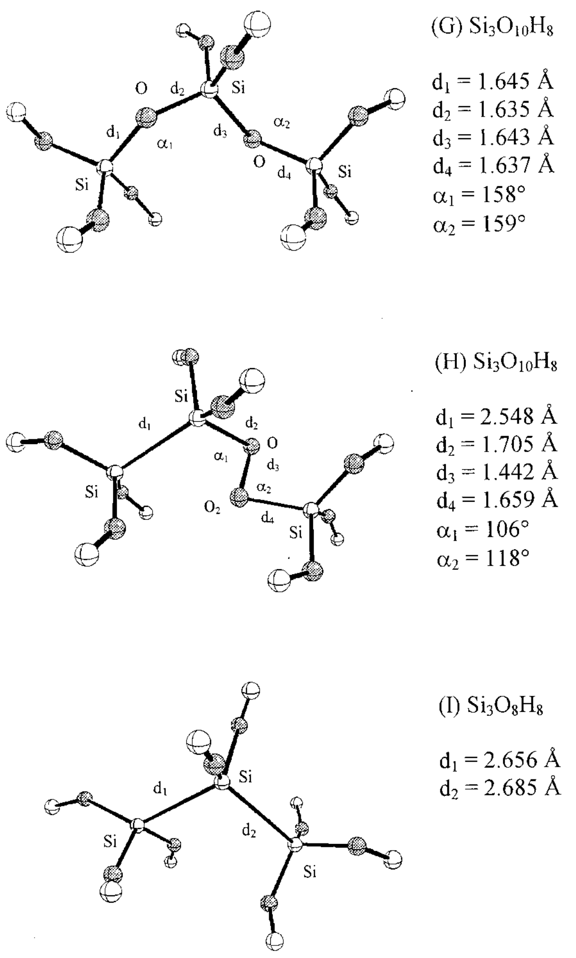

FIG. 3. $Si_3O_xH_8$ cluster models of local defects in α-quartz. (G) Regular crystal. (H) Frenkel defect. (I) Double oxygen vacancy. Geometrical parameters computed at the HF/HF(d) level (see text).

atoms. Other clusters have been designed to investigate various defects, Fig. 1–4, as well as Ge-doped silica, Figs. 5 and 6. Also for the defective structures, the cluster geometries have been fully optimized with the boundary condition that the position of the saturating H atoms is fixed. This means that only local relaxation effects have been considered; long-range lattice relaxation is not included. This may be particularly important for charged defects like the E' centers. However, a comparison of clusters of various size reveals only a moderate dependence of the geometrical parameters of the neutral defects on the cluster size; typical uncertainties in bond length are of the order of 3–4 %.

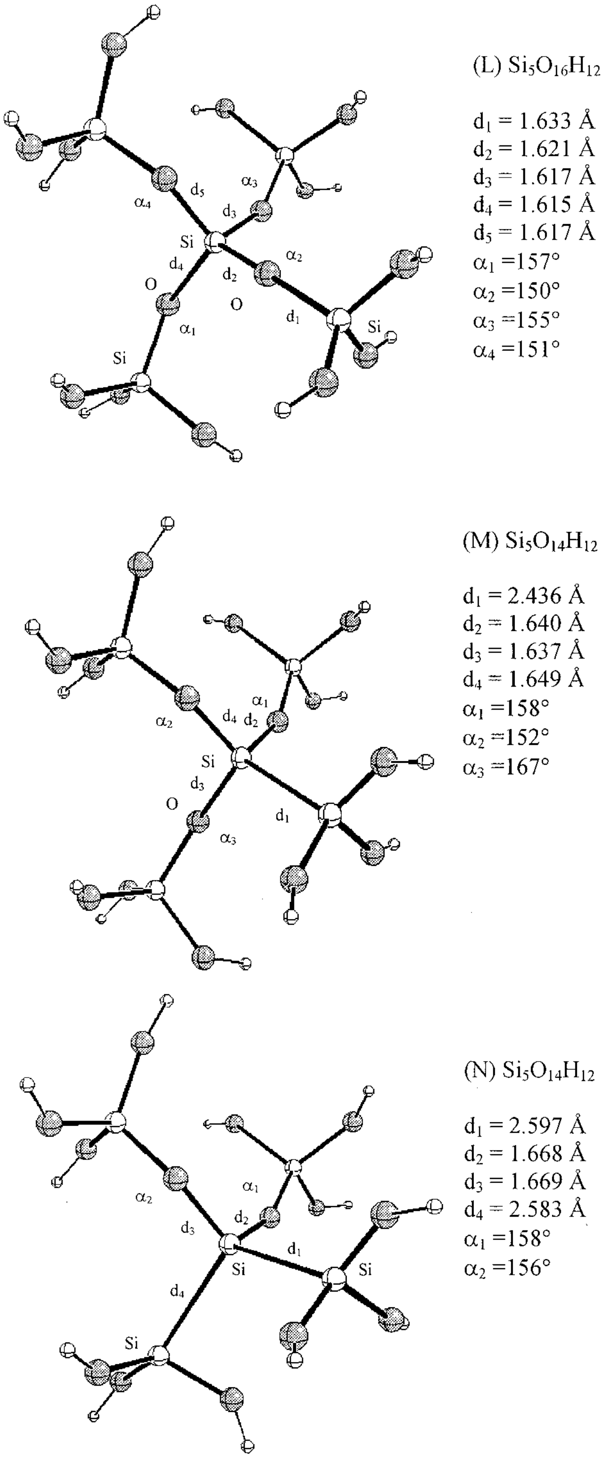

FIG. 4. $Si_5O_xH_{12}$ cluster models of local defects in α-quartz. (L) Regular crystal. (M) Single oxygen vacancy. (N) Double oxygen vacancy. Geometrical parameters computed at the HF/HF(d) level (see text).

B. Correlation effects

The HF cluster wave functions are sufficiently accurate for the description of geometrical parameters but the determination of dissociation energies requires the inclusion of electron correlation. Various techniques have been developed to include correlation effects starting from an HF wave function. Each method presents advantages and disadvantages, and the final choice depends on the problem under investigation. For the study of optical transitions of silica defects we recently used[13] a multireference configuration interaction approach, MR CI. However, MR CI is computationally expensive, is not size-consistent, and the geometry optimization at this level represents a formidable task. (A quantum-mechanical method is size-consistent when the energy and hence the energy error in the calculation increases in proportion to the size of the molecule. This is particularly important in the calculation of dissociation energies since a method that is not size consistent gives a total energy for a

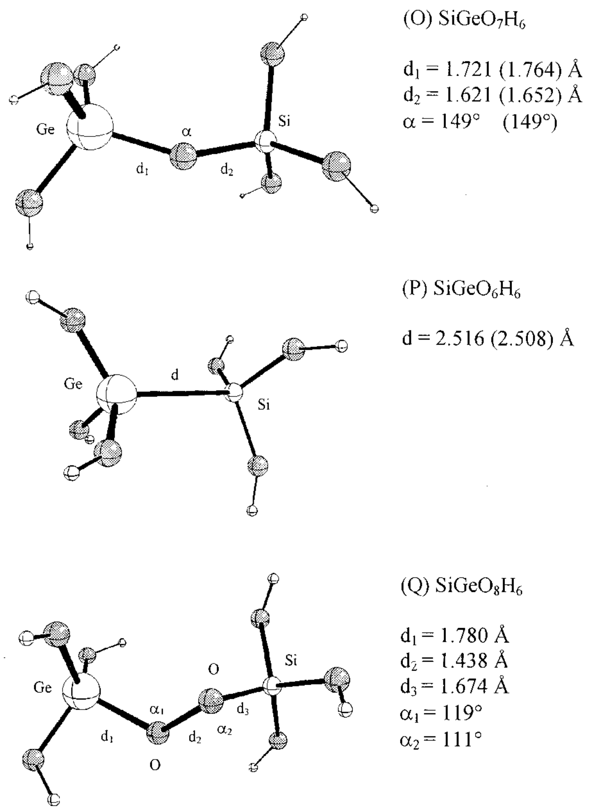

FIG. 5. $SiGeO_xH_6$ cluster models of local defects in Ge-doped silica. (O) Regular crystal. (P) Single oxygen vacancy. (Q) Peroxyl group. Geometrical parameters computed at the HF/HF(d) level (see text). Results at the MP2/MP2(d) level are in parentheses.

system of two units at very large distance which differs from the sum of the energies of the two isolated units.) Mølller-Plesset perturbation theory at second order, MP2, offers several advantages compared to the more elaborate MR CI approach. In particular it is size-consistent and it allows the geometry optimization at correlated level with analytical gradients. Therefore, we have performed MP2 calculations to determine the formation energies ΔE of a vacancy. The sign notation is such that a positive ΔE refers to an endothermic process. For the smaller clusters we have performed a full geometry optimization of the defect at both HF and MP2 levels, see Figs. 1 and 4. In general, however, the optimal geometries are very similar in the two approaches and single point MP2 calculations based on the HF minimum geometry give basically the same ΔE as for a fully optimized MP2 structure (see below). Therefore, for larger clusters where the full MP2 optimization becomes computationally very demanding we have performed single point MP2 calculations at the HF optimal geometry. The errors introduced by this procedure do not exceed 0.1–0.2 eV. We use the following notation to distinguish between the various cases: HF/MP2 indicates that the final energy has been evaluated at MP2 level based on the optimal HF geometry; MP2/MP2 means that the energy is that of a fully optimized structure at MP2 level. Furthermore, we indicate the inclusion of d functions on Si and O basis sets by (d,d'). Therefore, the HF/MP2 (d,d') notation indicates a single point MP2 calculation including d functions on both Si and O atoms involved in bond breaking based on the HF optimal geometry. MP2/MP2(d) refers to a MP2 geometry optimization with d functions on Si but not on O. All the calculations were performed with the HONDO 8.5 program package.[35]

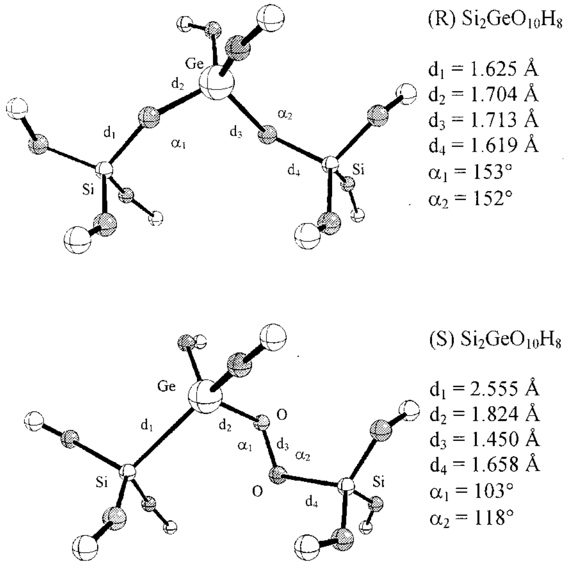

FIG. 6. $Si_2GeO_xH_8$ cluster models of local defects in Ge-doped silica. (R) Regular crystal. (S) Frenkel defect. Geometrical parameters computed at the HF/HF(d) level (see text).

III. GEOMETRICAL PARAMETERS

In Figs. 1–6 we report the structure and the relevant bond distances and bond angles for a series of defects in pure and Ge-doped silica. The geometrical parameters have been obtained at the HF/HF(d) level by full geometry optimization. The computed distances are expected to be reasonably close to the experimental ones. For comparison, at the HF/HF(d) level the equilibrium distances of SiO, GeO, and O_2 diatomic molecules, 1.502, 1.603, and 1.207 Å, respectively, are very close to the experimental values (SiO, 1.510 Å; GeO, 1.625 Å; O_2, 1.207 Å).[36] The computed long and short Si—O bond lengths obtained with the minimum $Si_2O_7H_6$ cluster, 1.630 and 1.620 Å, respectively, are only slightly longer than the experimental values of 1.614 and 1.605 Å for α-quartz.[32] The d polarization functions on Si and O have virtually no effect on the optimized geometrical parameters. Also the optimization at a correlated level, MP2/MP2(d), gives bond lengths which are very similar to the HF ones, see Figs. 1 and 4. Less satisfactory is the agreement for the bond angles. In fact, with the $Si_2O_7H_6$ cluster we compute a Si—O—Si bond angle of 155° which is 8% larger than the angle of 144° measured in α-quartz by x-ray diffraction.[32] In this respect, it is worth noting that the MP2 angle, 151°, Fig. 1, is closer to the experimental one. The differences in bond angles can be due to intermediate range ordering effects not included in a cluster wave function.

The oxygen removal from the $Si_2O_7H_6$ minimum cluster model, see Fig. 1(A), results in the formation of a direct Si—Si bond of 2.53 Å, Fig. 1(B). This result is only moderately dependent on the cluster size; in fact, with the $Si_5O_{15}H_{12}$ cluster, Fig. 4(M), we found a similar Si—Si dis-

TABLE I. Dissociation energies D_e of SiO, GeO, O_2, and $Si(OH)_4$ molecules.

Method[a]	D_e(Si—O) (eV)	D_e(Ge—O) (eV)	D_e(O—O) (eV)	$D_e[(OH)_3Si—OH]$ (eV)
HF/HF(d)	4.19	2.69	−0.81	4.81
HF/MP2(d)	7.38	6.10	3.12	5.44
MP2/MP2(d)	7.47	6.21	3.65	
HF/HF(d,d')	4.59	3.29	1.22	4.79
HF/MP2(d,d')	8.01	6.80	4.80	5.65
MP2/MP2(d,d')	8.09	6.90	5.04	
Experimental (Ref. 36)	8.26	6.78	5.11	6.26[b]

[a] See text for definitions.

[b] From *ab initio* MP4 calculations, Ref. 38.

tance, 2.44 Å. The formation of a peroxyl group, Fig. 1(C), results in an O—O bond length of 1.43 Å and in elongated Si—O bonds. Because of the strain induced by the presence of the —O—O— peroxyl group, the Si atoms flatten out to some extent. This is found also using the larger $Si_3O_{10}H_8$ cluster, Fig. 3(H), which models a Frenkel defect, i.e., an O vacancy adjacent to a peroxyl group. In this case we notice that the Si—Si distance in the oxygen vacancy, 2.55 Å, is almost identical to that computed for the isolated defect, 2.53 Å. The similarity of the geometrical parameters in Figs. 1(B) and 1(C) and Fig. 3(H) indicates a small mutual influence of the two adjacent defects and further support the independence of the results on cluster size.

The E' center, Fig. 1(D), is a positively charged center and the amount of geometry relaxation is expected to be large. The cluster used, Fig. 1(D), is too small to reproduce the long-range geometrical distortion of this site. Calculations with much larger clusters are in progress.[37] As already noticed by other authors,[23] both Si atoms assume a nearly planar coordination although the unpaired electron is preferentially localized on one side. This is shown by the values of the EPR hyperfine coupling constants which show a substantial localization of the spin density on a Si atom.[23,27]

The Si—O distance in the $\equiv$Si—O$^\bullet$ and $\equiv$Si—O—O$^\bullet$ radicals, Figs. 2(E) and 2(F), about 1.68–1.69 Å, is longer than that of a normal Si—O bond in α-quartz; on the other hand, the O—O distance in the peroxyl radical, 1.38 Å, Fig. 2(F), is shorter than in the peroxyl group, 1.43 Å, Fig. 1(C). The results have been obtained with small clusters and some care is necessary in the analysis of the data on $\equiv$Si—O$^\bullet$ and $\equiv$Si—O—O$^\bullet$ radicals. Therefore, we do not further discuss these defects. The electronic structure and EPR parameters of paramagnetic defects will be addressed in detail using larger cluster models in a separate publication.[37]

The structure of a double oxygen vacancy has been computed with two clusters, $Si_3O_8H_8$, Fig. 3(I), and $Si_5O_{14}H_{12}$, Fig. 4(N). Of course, the smaller model allows only a partial relaxation of the central Si atom to respond to the formation of the double vacancy; the resulting Si—Si distances, ≈2.67 Å, are about 0.1 Å longer than in the single oxygen vacancy. Using the larger $Si_5O_{14}H_{12}$ cluster, however, we found only a small change in the Si—Si distance, 2.60 Å, Fig. 4(N). The longer Si—Si distance in the double oxygen vacancy compared to the single vacancy reflects the higher strain in the structure due to the removal of two lattice oxygens.

We consider now the local geometrical structure of defects in Ge-doped silica. Ge has slightly larger atomic radius than Si, 1.52 against 1.46 Å. Therefore, longer distances are expected in the Si—Ge or Ge—O bonds compared to the corresponding Si—Si or Si—O bonds. For instance, the diatomic gas-phase molecule GeO is 0.1 Å longer than the isovalent SiO molecule.[36] Indeed, the Ge—O bond for a Ge substitutional impurity in α-quartz is 1.70–1.72 Å depending on the cluster model used [see Figs. 5(O) and 6(R)], i.e., 0.05–0.10 Å longer than in the corresponding pure SiO_2 structure. On the other hand, the Si—Ge distance in an oxygen vacancy involving the Si—O—Ge bond breaking, ≈2.5 Å, see Figs. 5(P) and 6(S), is surprisingly close to that of a Si—Si bond. This result can be of considerable importance for the study of optical transitions in crystalline and amorphous silica. In fact, it has been shown that the optical transition of an oxygen vacancy, occurring at about 7.6 eV in α-quartz, is sensitive to the Si—Si (hence to the Si—Ge) distance.[13] Finally, we notice that, apart from the slightly longer Ge—O bond, there is no significant difference in the geometry of a peroxyl group or of a Frenkel defect in Ge-doped compared to pure silica [cf. Figs. 5(Q) and 6(S) with Figs. 1(C) and 3(H)].

IV. FORMATION ENERGIES

A. Accuracy of the method

In order to establish the accuracy of the computed formation energies we have determined the bond dissociation energies for a few gas-phase molecules for which thermodynamic data or state-of-the-art calculations exist. Since we are particularly interested in the Si—O, Ge—O, and O—O bonds we have considered the SiO, GeO, O_2, and $Si(OH)_4$ molecules. The experimental dissociation energies D_e of SiO, GeO, and O_2 are 8.26, 6.78, and 5.11 eV, respectively.[36] At the MP2/MP2(d,d') level the computed D_e's are 8.09, 6.90, and 5.04 eV, respectively, in excellent agreement with the experiment, Table I. At the HF/MP2(d,d') level, the approach followed for the determination of the formation energies, the computed D_e's, 8.01 eV (SiO), 6.80 eV (GeO), and 4.80 eV (O_2), are also reasonably close to the measured ones with errors of less than 6%, Table I. To estimate the accuracy in the description of single Si—O bonds we have computed the D_e for the process $Si(OH)_4 \rightarrow (OH)_3Si^\bullet + OH^\bullet$. An estimate of 6.3 eV has been reported for this bond strength based on high-quality calculations;[38] this latter value is slightly larger than our $D_e = 5.7$ eV computed at the HF/MP2(d,d') level. In general, we can conclude that the

TABLE II. Defect formation energy ΔE for an oxygen vacancy in α-quartz.

Regular site	Oxygen vacancy	Basis set Si	Basis set O	Theoretical level[a]	ΔE (eV)
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ	DZ	HF/HF	5.5
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ+d	DZ	HF/HF(d)	6.6
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ+d	DZ+d	HF/HF(d,d')	6.7
$Si_5O_{16}H_{12}$[b]	$Si_5O_{15}H_{16}$	DZ+d	DZ	HF/HF(d)	6.7
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ	DZ	HF/MP2	7.0
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ+d	DZ	HF/MP2(d)	7.9
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ+d	DZ	MP2/MP2(d)	7.9
$Si_2O_7H_6$	$Si_2O_6H_6$	DZ+d	DZ+d	HF/MP2(d)(d')	8.5

[a] See text for definitions.

[b] Basis DZ+d on Si and DZ on O involved in bond breaking, 3-21G on all remaining atoms.

bond strength in these simple molecules is properly described although it may be slightly underestimated.

The previous results refer to small gas-phase molecules, while we are interested in the energetics of processes occurring in solid state. Therefore, before discussing the computed formation energies it is useful to consider computational aspects with direct impact on the energetics. To this end we consider the formation energy of an oxygen vacancy in pure SiO_2; we first analyze the effect of basis set and cluster size. Let us consider the minimum $Si_2O_7H_6$ cluster, Table II. At the HF/HF level, without d functions on O and on Si, we found a ΔE of 5.5 eV. This value compares rather well with the $\Delta E \approx 5$ eV found with a more elaborate embedding approach using a similar basis set (with no d polarization functions).[18] By adding the d function on Si, HF/HF(d), ΔE becomes 6.6 eV; when also the d function on O is included, HF/HF(d,d'), ΔE becomes 6.7 eV showing that at the one-electron level the d function on Si is considerably more important than the d on O.

A possible source of error in the computed formation energies is the dependence of ΔE on the cluster size. For our study we used relatively small clusters but we also considered larger models like the $Si_5O_{16}H_{12}$ cluster, Fig. 4(L). This cluster is derived from the smaller $Si_2O_7H_6$ cluster by replacing three embedding H atoms with $Si(OH)_3$ groups, Table II. For the ≡Si—O—Si≡ unit involved in bond breaking we used the same basis set as in $Si_2O_7H_6$ while all the other atoms were treated with a smaller basis 3-21G basis set.[39] With this larger fully optimized cluster ΔE at the HF/HF(d) level is 6.7 eV, i.e., almost coincident with that obtained with the smaller model. Therefore, we can safely conclude that the size of the cluster has virtually no effect on the binding energies, at least for neutral defects (charged defects can induce substantial polarization of the lattice which is not taken into account by a small cluster).

We consider now the importance of correlation effects. The formation energy computed with the minimum $Si_2O_7H_6$ cluster at the HF/MP2 level is 7.0 eV, Table II, i.e., 1.5 eV larger than at the one-electron level. With d functions on Si, HF/MP2(d), ΔE becomes 7.9 eV, Table II. We repeated the calculation by performing a full MP2 geometry optimization, MP2/MP2(d), but we found no change in the formation energy which remains 7.9 eV. This is due to the fact that the regular structure and the O vacancy are stabilized by the same extent by the addition of the d orbitals on Si. Finally, we added a d function on O, HF/MP2(d,d'), and we obtained $\Delta E = 8.5$ eV. This value represents our best estimate of the formation energy of an oxygen vacancy; it is consistent with the recent proposal of Boureau and Carniato of a formation energy >7.3 eV.[19] These data also explain the discrepancy between the other *ab initio* value reported in the literature, ≈5 eV,[18] and the experimental guess;[19] this is simply due to the lack of d functions on Si and O and of correlation effects. The Si and O d functions cause an increase of ΔE by ≈1–1.5 eV, whereas correlation effects contribute by about 1.4–1.5 eV. The two terms are roughly additive, and their simultaneous inclusion is essential in order to obtain reliable formation energies of defects in silica. In the following, we report only our best estimates of the formation energies obtained at the HF/MP2(d,d') level.

B. Point defects in pure SiO_2

The energies discussed in the paper are defined with respect to the formation of ground-state atomic oxygen, ^3P. However, it is likely that the creation of oxygen vacancies in the bulk of SiO_2 is accompanied by the formation of molecular oxygen, O_2. The experimental dissociation energy of O_2 is 5.1 eV;[36] the computed one at the HF/MP2(d,d') level is 4.80 eV, Table I. Therefore, defect formation energies with respect to O_2 can be easily derived by considering an energy gain of 4.8 eV for the process $2O \rightarrow O_2$.

HF/MP2(d,d') formation energies for a series of defects are reported in form of thermodynamic Born-Haber cycle in Fig. 7. As discussed in the previous paragraphs, the forma-

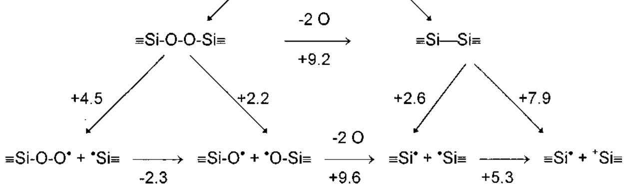

FIG. 7. Formation energies of defects in pure silica from $Si_2O_xH_6$ cluster models. Values in eV obtained at the HF/MP2(d,d') level (see text). See Figs. 1 and 2 for geometrical structures.

tion energy of an O vacancy is 8.5 eV. This process involves the rupture of two Si—O bonds, with formation of ≡Si$^\bullet$ radicals, and the consequent recombination of the two dangling bonds to give a direct Si—Si covalent bond. The energy gain associated to this latter process is 2.6 eV, see Fig. 7. Therefore, one can estimate the bond dissociation energy of the Si—O bond in α-quartz as 2 D_e (Si—O)=8.5 eV +2.6 eV and D_e(Si—O)=5.5 eV. In the crystal, the formation of an oxygen vacancy can be associated with that of a peroxyl group giving rise to a Frenkel defect, Fig. 3(H). The addition of an isolated O atom to the ≡Si—O—Si≡ bond, leading to a peroxyl unit, corresponds to an energy gain of 0.7 eV, Fig. 7. This is due to the relatively strong O—O bond in the peroxyl group which compensates for the increased strain in the lattice. The removal of the 2 O atoms from the ≡Si—O—O—Si≡ peroxyl group to form an oxygen vacancy, ≡Si—Si≡, requires 9.2 eV, Fig. 7. This energy is reduced to 4.4 eV if the process is considered with respect to the formation of an O_2 molecule.

The breaking of the Si—O bond in ≡Si—O—O—Si≡ costs 4.5 eV; this is about 1 eV less than the energy required to break a Si—O bond in a ≡Si—O—Si≡ chain, ≈5.5 eV. Thus, the strength of the Si—O bond depends in a marked way on the neighboring groups. The breaking of the O—O bond in ≡Si—O—O—Si≡ to form two ≡Si—O$^\bullet$ radicals requires only 2.2 eV, Fig. 7; this is much less than the D_e of O_2 and is also less than the energy required to break the Si—O bond. This suggests that radiation or thermal damage in pure SiO_2 will result in the preferential formation of ≡Si—O$^\bullet$ radicals rather than of peroxyl radicals, ≡Si—O—O$^\bullet$. These centers, however, could easily form by direct combination of O_2 with ≡Si$^\bullet$ centers.

The breaking of the ≡Si—O$^\bullet$ bond to form a ≡Si$^\bullet$ radical and an O atom costs 4.8 eV. This value is intermediate between that of a ≡Si—O—Si≡ structure, 5.5 eV, and that of a Si—O bond in a peroxyl linkage, ≡Si—O—O—Si≡, 4.5 eV. The ≡Si$^\bullet$ defect can also be obtained by direct breaking of the ≡Si—Si≡ bond of an oxygen vacancy. In this case, the formation energy is of 2.6 eV, Fig. 7. Much higher is the energy necessary to form an E' center consisting of a ≡Si$^\bullet$ radical and a ≡Si$^+$ ion; this is 7.9 eV starting from a neutral oxygen vacancy, ≡Si—Si≡, and can be viewed as the sum of two contributions, the energy required to break the Si—Si bond, 2.6 eV, and the ionization energy of the ≡Si$^\bullet$ radical, 5.3 eV, Fig. 7. However, the calculation of formation energies of charged defects with cluster models does not include long-range electronic and structural relaxation effects that can have non-negligible effects on the energetics.

In Fig. 8 we report the formation energies of a Frenkel defect, ≡Si—Si—O—O—Si≡, and of a double oxygen vacancy, ≡Si—Si—Si≡. For these calculations we used a larger cluster, $Si_3O_{10}H_8$, Fig. 3. The Frenkel defect is 7.6 eV less stable than the regular structure; this energy corresponds to the cost of breaking two Si—O bonds, ≈11 eV, minus the gain due to the formation of the O—O bond, ≈0.7 eV, and of a Si—O bond, ≈2.6 eV. The energies involved in the process are very close to those computed with the smaller clusters for an isolated O vacancy and a peroxyl group. This further shows that the results are not (or very weakly) dependent on the cluster size and that the bond energies are practically transferable from one structure to another. For the same reason, the energy necessary to form a double oxygen vacancy from a regular structure, 17.4 eV, is almost exactly twice the energy involved in the formation of a single vacancy, Fig. 8. This is of course a very large energy, but the net cost is substantially reduced if one assumes the formation of an O_2 molecule (in this case ΔE becomes 12.6 eV).

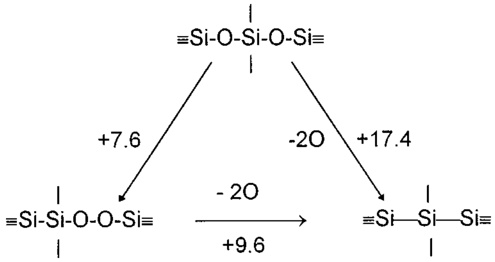

FIG. 8. Formation energies of defects in pure silica from $Si_3O_xH_8$ cluster models. Values in eV obtained at the HF/MP2(d,d') level (see text). See Figs. 3 for geometrical structures.

C. Point defects in Ge-doped SiO_2

The trends observed in the stability of the various defects of pure SiO_2 are found also when Ge substitutional impurities are present. The main difference, however, is that the Ge—O bond is weaker than the Si—O one. This is well documented by the difference in stability of the corresponding diatomic molecules, Table I: the D_e of SiO is about 20% larger than that of GeO. In a similar way, the computed formation energy of an oxygen vacancy involving a Ge substitutional impurity is 7.5 eV, see Fig. 9, compared to the 8.5 eV computed for pure SiO_2. This is an important result since it suggests that the damage caused by γ rays in Ge-doped silica will result in the preferential formation of oxygen vacancies involving a Si-Ge pair rather than a Si-Si pair. Of course, this is not restricted to the single oxygen vacancy, but it applies also to other defects like a Frenkel defect or a double oxygen vacancy, see Fig. 10. For instance, the formation of a Frenkel pair costs only 6.5 eV, i.e., 1.1 eV less than in pure silica. In conclusion, we provide strong evidence that the presence of Ge atoms in the bulk of SiO_2 leads to a preferential breaking of the Ge—O bonds with respect to the Si—O ones and to an increase in the concentration of the defects due to interaction with radiation.

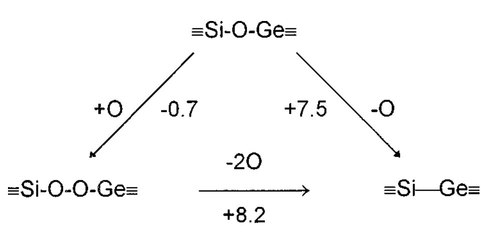

FIG. 9. Formation energies of defects in Ge-doped silica from $SiGeO_xH_6$ cluster models. Values in eV obtained at the HF/MP2(d,d') level (see text). See Figs. 5 for geometrical structures.

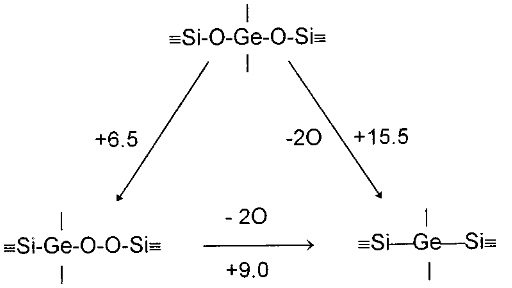

FIG. 10. Formation energies of defects in pure silica from $Si_2GeO_xH_8$ cluster models. Values in eV obtained at the HF/MP2(d,d') level (see text). See Figs. 6 for geometrical structures.

D. The Si vacancy

It has been suggested that ion bombardment of silica can lead to the creation of Si vacancies.[40] Of course, given the relatively strong Si—O bond, the rupture of four of such bonds is a process which requires a large amount of energy. The removal of a lattice Si atom results in the formation of four $\equiv$Si—O$^\bullet$ radicals. This process has been studied using the larger $Si_5O_{16}H_{12}$ cluster and the corresponding defective cluster (with one missing Si atom). The cluster was treated with a smaller basis set, 3-21G, except for the Si and O atoms involved in bond breaking. For these atoms we used a DZ basis set on both O and Si atoms. We found a formation energy for the Si vacancy of $\approx$17 eV at the HF level. With a similar treatment the Si—O bond dissociation energy computed with the smaller $Si_2O_7H_6$ cluster is $\approx$4 eV. The Si vacancy formation energy corresponds roughly to four times the Si—O bond dissociation energy. Given the absence of correlation effects, this value is certainly underestimated, by about 35%. Therefore, a reasonable estimate for the Si vacancy formation energy is about 23 eV. This value however will be reduced by the recombination of the $\equiv$Si—O$^\bullet$ radicals to form two pairs of peroxyl groups. The energy gain for the process 2$\equiv$Si—O$^\bullet \to \equiv$Si—O—O—Si$\equiv$ is of 2.2 eV, Fig. 6; this means that the formation energy for a Si vacancy will be close to 18–19 eV. This is a very large energy, and the concentration of these defects caused by radiation damage is expected to be low.

V. CONCLUSIONS

We have determined by means of accurate *ab initio* calculations the formation energies of a series of point defects in pure and Ge-doped α-quartz. We have shown that correlation effects and inclusion of *d* orbitals on Si and O are essential for a proper description of the Si—O chemical bond. The strength of a Si—O bond in crystalline α-quartz is about 5.5 eV. The creation of an O vacancy implies the rupture of two of these bonds, with a total cost of 11.1 eV, partially compensated by the formation of a direct Si—Si bond with an energy gain of 2.6 eV. Therefore, the computed formation energy for an O vacancy is 8.5 eV. This value is consistent with recent thermodynamic arguments which estimate a lower bound for the defect formation energy of 7.3 eV.[19] The insertion of a free O atom into a $\equiv$Si—O—Si$\equiv$ structure results in a peroxyl group, $\equiv$Si—O—O—Si$\equiv$, with an energy gain of 0.7 eV. It is important to note, however, that the recombination of two lattice O atoms to form O_2 is accompanied by an energy gain of $\approx$5 eV. It is very likely that this species forms and remains trapped into the cavities of the crystalline structure. Indeed, very recently the presence of interstitial O_2 molecules in silica glass has been detected by means of optical spectroscopy.[41] The rupture of the —O—O— bond of the peroxyl group, 2.2 eV, is found to be easier than the breaking of the Si—O bonds whose strength goes from $\approx$4.5 eV in $\equiv$Si—O—O—Si$\equiv$, to 4.8 eV in $\equiv$Si—O$^\bullet$, and 5.5 eV in $\equiv$Si—O—Si$\equiv$. Therefore, we observe a dependence of the Si—O bond dissociation energy on the local electronic structure. The displacement of a lattice O to form a Frenkel defect, $\equiv$Si—Si—O—O—Si$\equiv$, requires a large amount of energy, about 8 eV, as the consequence of the high Si—O bond dissociation energy.

The replacement of Si by Ge in the SiO_2 lattice results in weakened Ge—O bonds compared to the Si—O counterparts. Therefore, we expect that radiation damage in Ge-doped silica will result in the preferential breaking of the lattice sites occupied by Ge atoms. Finally, we have also estimated the formation energy of a Si vacancy. This is very high, around 20 eV, consistent with the fact that the removal of a lattice Si implies the rupture of four Si—O bonds. High-energy processes, like ion bombardment, are probably necessary to form appreciable concentrations of these defects.

ACKNOWLEDGMENTS

This work has been supported by the Italian Ministry of University and Research. The authors thank G. Boureau (Paris), M. Martini, A. Paleari, G. Spinolo, and A. Vedda (Milano) for several useful discussions.

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