PHYSICAL REVIEW B VOLUME 42, NUMBER 15 15 NOVEMBER 1990-II

Models of the self-trapped exciton and nearest-neighbor defect pair in SiO_2

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(Received 1 December 1989; revised manuscript received 18 June 1990)

The adiabatic potential surface for triplet exciton self-trapping and Frenkel-defect pair creation in SiO_2 has been studied with use of a periodic supercell model and a self-consistent intermediate neglect of the differential overlap method for open shell. The results obtained confirm completely the self-trapped-exciton (STE) model obtained earlier [A. Shluger, J. Phys. C **21**, L431 (1988)], making it possible to interpret in greater detail the nature of its optical absorption and luminescence. It is shown that in the case of the SiO_2 structure considered (the ideal β-cristobalite) the formation of nearest-neighbor defect pair (NNDP) from the STE state requires surmounting an energy barrier of about 1 eV. The electronic component of a NNDP comprises two E'-like centers localized on two silicons surrounding a single oxygen vacancy, one of which is perturbed by the hole component of the —Si—O—O—Si— "peroxide bridge." STE and NNDP are shown to belong to the same adiabatic energy surface with the minima corresponding to NNDP to be deeper than that for STE. Calculated spectra of optical transition energies of NNDP include two transitions corresponding to electronic-component excitation (6.1 eV for one E' center and 5.6 eV for another E' center, perturbed by a "peroxide bridge"), charge-transfer transition from a E' center to the peroxide bridge ($E_{\max}=4.9$ eV), and hole-component excitation ($E_{\max}=1.7$ eV). The driving forces of the triplet exciton self-trapping and Frenkel-defect formation are discussed.

I. INTRODUCTION

Irrespective of the fact that self-trapped triplet excitons in crystalline and amorphous SiO_2 have been established experimentally and investigated in a series of works,[1–4] their electronic and spatial structure is still subject to discussion. The common feature of all the models considered is that self-trapping is due to the displacement of an oxygen ion from a regular lattice site into an interstitial site[1,3–5] with the formation of an E' center at one of the silicon ions neighboring the vacancy. Deexcitation of an exciton in both crystalline (c-) and amorphous (a-) SiO_2 gives rise to luminescence, whose spectrum and temperature dependence have been investigated in detail.[1,5–8] The excitation spectrum of the exciton luminescence in c-SiO_2 has been carefully measured in a recent work.[9] The initial state of the luminescence has a lifetime exceeding 1 ms at low temperature. The optical absorption of a- and c-SiO_2 from that state has also been measured and found to be accompanied by the annihilation of excitons.[6,7] The self-trapping of excitons brings about a large macroscopic volume change of the samples.[10] The magnetic-resonance parameters of the triplet self-trapped exciton (STE) in c-SiO_2 have been measured in Ref. 11 using optically detected magnetic resonance (ODMR).

The formation of defects (E' centers) by electronic excitation, which is assumed to be related to the STE decay, has only been observed in a-SiO_2.[3,8,12,13] Their production efficiency does not apparently exceed 0.01 of the number of STE's formed.[3]

The experimental data accumulated so far do not, however, allow drawing even a qualitative conclusion on the spatial atomic structure of the STE, nor it is yet possible to explain the experimental data in terms of a unified model. A theoretical work by one of the present authors[14] based on a self-consistent calculation of the electronic and spatial structure of the triplet STE in c-SiO_2 (β-cristobalite structure) has shown that exciton self-trapping in this system is accompanied by weakening of one of the two Si—O bonds of an oxygen, as well as with a small ($\simeq 0.3$ Å) displacement of the oxygen ion towards an interstitial position. The distribution of electronic and spin densities at the minimum of the adiabatic energy surface, as calculated in Ref. 14, corresponds to the formation of a mutually-perturbing nonbridging oxygen (hole component) and an E'-like center (electronic component of the exciton). The exciton luminescent energy obtained in Ref. 14 is found to agree well with the experimental energy. The distribution of the spin density found made it possible to explain in a semiquantitative way the large value of the zero-field splitting parameter D, as obtained on interpreting the ODMR data. In a recent work[15] based on an *ab initio* molecular-orbital (MO) linear combination of atomic orbitals (LCAO) calculations of the electronic and spatial structure of a small cluster, simulating the α-quartz structure, the same STE model has virtually emerged. Additionally computed have been some magnetic resonance parameters, the luminescence polarization, and the volume change. All these quantities have agreed with the experimental data. An important conclusion from this work is that irrespective of the stiffness of the Si—O bond, a small displacement of an oxygen ion is accompanied by small shifts of a number of surrounding ions, which determines as a whole the large volume change of the sample in the STE state.[15]

The above-described results shine light on the possible STE model in *c*-SiO_2. Self-trapped excitons in some nonmetallic solids like alkali halides are considered to be the precursor of vacancy-interstitial pairs (defect pairs): a STE and a defect pair are the configurations at the two neighboring minima of the adiabatic potential-energy surface separated by a potential barrier. Since defects are known to be generated in *a*-SiO_2 by electronic excitation,[3] it is likely that a STE may have a decay path to a defect pair. An important step in that direction has been taken in Ref. 16, where on the basis of a theoretical analysis of the temperature dependence of the exciton-luminescence lifetime in *a*-SiO_2 the barrier height has been estimated for the transition from the triplet exciton ground state to the configuration of a nearest defect pair. However, the method of quantum-rate theory used does not give enough quantitative information on the structure of the defect pair. In this way the question remains open. Clearly, one of the pair components is the E' center, whose optical absorption is observed in transient experiments induced by irradiation with an electron pulse.[1,5–8] Another essential point is the occurrence of a STE luminescence on optical excitation of the so-called short-lived E' centers, as investigated in Ref. 8.

In the present work, on the basis of a theoretical periodic supercell model, free from the familiar limitations of the cluster models, we have investigated subsequently the electronic and spatial structure and the optical characteristics of STE and a Frenkel pair in SiO_2. The results obtained confirm completely the exciton model, obtained earlier,[14] making it possible to interpret in greater detail the nature of its optical absorption and luminescence. It is shown that in the case of the SiO_2 structure considered (the ideal β-cristobalite) the formation of a nearest defect pair requires surmounting an energy barrier of about 1 eV. The electronic component of a pair comprises two E'-like centers localized on two silicon ions surrounding a single oxygen vacancy, one of which is perturbed by the hole-component —Si—O—O—Si— "peroxide bridge."

II. DETAILS OF COMPUTATION

Our purpose is to investigate the possibility of self-trapping of a triplet exciton, calculate its electronic and spatial structure, its optical characteristics, and to search for decay modes in Frenkel defect pairs. One of the ways of solving this problem is to compute and investigate the adiabatic potential-energy surfaces of the crystal excited states based on the multielectron theory of defect-containing crystals. From the viewpoint of simulating the exciton self-trapping the original equivalency of the perfect lattice sites is essential. This condition is met by the periodic model, which, however, has its limitations.

The main limitation is the mutual perturbation of periodically arranged defects. It can be overcome by considering larger cells. Such an approach, however, encounters enormous computational time in the case of applying nonempirical band methods (a detailed analysis can be found in Ref. 17). An alternative approach, which is adequate from the viewpoint of our present purpose, is to use the supercell model [based on the large unit cell (LUC) method[18,19]], as well as the approximate MO LCAO. For the quality of the latter we have chosen the intermediate neglect of differential overlap (INDO) method, which has nicely recommended itself in previous computational work on defects[20–22] and STE (Ref. 14) in SiO_2. Combining the LUC method with the relatively simple computational INDO scheme it is possible to investigate in sufficient detail the complicated adiabatic surfaces at the excited states of the crystal within the framework of the unrestricted Hartee-Fock (UHF) method.

The basic computational relations for calculating the total energy of the crystal within the framework of the LUC method have been proposed in Refs. 17–19 and 23. Below, we will briefly concentrate on the details of the computational scheme employed presently, considering for simplicity the equations for the closed-shell case.

The basic idea of the LUC model is in computing the electronic structure of the unit cell extended in a special manner (large unit cell) at $\mathbf{k}=\mathbf{0}$ in the narrowed Brillouin zone (NBZ), which is equivalent to a band calculation at those BZ $\mathbf{k}$ points, which transform to the NBZ center on extending the unit cell.[18,19] As indicated by numerous computations, in ionic and ionic-covalent crystals a fourfold- or eightfold-symmetric extension of the unit cell (equivalent to a band calculation at three special points of the BZ) proves completely sufficient for adequately reproducing the distribution of the electronic density in the perfect crystal.[19]

The electronic density-matrix elements in the atomic-orbital (AO) basis of the LUC method are

$$P^{0l}_{\mu\nu}=\frac{1}{N}\sum_{k\in \mathrm{BZ}}\rho_{\mu\nu}(\mathbf{k})e^{i\mathbf{k}\cdot l}\ , \tag{1}$$

where $\rho(\mathbf{k})$ are the density-matrix elements in the basis of Bloch's combinations of AO's, l is the Bravais vector of the lattice, as built up by the LUC, while N is the number of LUC's in the basic region of the crystal. The total electronic energy in this model is

$$E^{\mathrm{el}}_{\mathrm{LUC}}=\tfrac{1}{2}\sum_{\mu,\nu}\sum_{l}P^{0l}_{\mu\nu}(H^{0l}_{\mu\nu}+F^{0l}_{\mu\nu})\ , \tag{2}$$

where $F^{0l}_{\mu\nu}$ are the elements of Fock's matrix, while $H^{0l}_{\mu\nu}$ are the elements of the one-electron part of Fock's matrix in the AO basis. In the INDO approximation the latter are assumed proportional to the AO μ and ν overlap.[24] The elements of the overlap matrix rapidly diminish as the distance $r_{\mu\nu}$ is increased. For that reason, using the cutoff function introduced in Ref. 23,

$$\omega(r_{\mu\nu})\equiv P^{0l}_{\mu\nu}/\rho_{\mu\nu}(0)\ ,$$

where

$$\rho_{\mu\nu}(k)=\sum_{l} e^{-i\mathbf{k}\cdot l}P^{0l}_{\mu\nu} ,$$

the following approximations can be introduced for the LUC, whose size is large:

$$\sum_{l} P^{0l}_{\mu\nu}H^{0l}_{\mu\nu}=\rho_{\mu\nu}(0)\sum_{l} H^{0l}_{\mu\nu}\omega(r_{\mu\nu})\simeq\rho_{\mu\nu}(0)\sum_{l} H^{0l}_{\mu\nu} .$$

The second term in (1) can be represented as

$$\tfrac{1}{2}\sum_{\mu,\nu}\sum_{l} P^{0l}_{\mu\nu}F^{0l}_{\mu\nu}=N^{-1}\sum_{j=1}^{\text{occ}}\sum_{k\in\text{BZ}} \varepsilon_j(\mathbf{k})\simeq\sum_{j}^{\text{occ}}\varepsilon_j(0) .$$

Here $\varepsilon_j(\mathbf{k})$ are the eigenvalues of Fock's matrix, while occ is the number of occupied electronic states in the system. Now the total energy of the crystal is

$$E_{\text{LUC}}=\tfrac{1}{2}\sum_{A\neq B} Z_A Z_B(R^{00}_{AB})^{-1}+\tfrac{1}{2}\sum_{A\in\text{LUC}} E^A_c$$
$$+\sum_{j}^{\text{occ}}\varepsilon_j(0)+\tfrac{1}{2}\sum_{\mu,\nu\in\text{LUC}}\rho_{\mu\nu}(0)Q_{\mu\nu} , \qquad (3)$$

where

$$E^A_c=Z_A\sum_{l\neq 0}\sum_{B\in\text{LUC}}\left(Z_B(R^{0l}_{AB})^{-1}-\sum_{\mu\in B}\rho_{\mu\mu}(0)(v^{A0})^{ll}_{\mu\mu}\right) ,$$

$$Q_{\mu\nu}=\begin{cases} T^{00}_{\mu\mu}-\sum\limits_{A\in\text{LUC}} Z_A(v^{A0})^{00}_{\mu\mu}+\sum\limits_{l\neq 0} H^{0l}_{\mu\mu}, & \mu=\nu \\ \sum\limits_{l} H^{0l}_{\mu\nu}, & \mu\neq\nu. \end{cases}$$

Here $T^{00}_{\mu\mu}$ are the matrix elements of the kinetic-energy operator, $(v^{A0})^{ll}_{\mu\mu}$ are those of the electron-core interaction operator, R^{0l}_{AB} is the distance between the cores of atoms A and B, while Z_A and Z_B are their charges.

In the LUC method, the Hartree-Fock-Roothaan equations in INDO approximation have the form

$$\sum_{\nu\in\text{LUC}} F_{\mu\nu}c_{\nu j}(0)=\varepsilon_j(0)c_{\mu j}(0) , \qquad (4)$$

where $c_{\nu j}(0)$ are the LCAO coefficients in the LUC classification, while the elements of Fock's matrix are

$$F_{\mu\nu}=\tilde{H}_{\mu\nu}+\delta_{\mu\nu}C_{\mu\mu}+G_{\mu\nu}+A_{\mu\nu} .$$

The one-electron part of Fock's matrix is

$$\tilde{H}_{\mu\nu}=\begin{cases} T^{00}_{\mu\mu}-Z_A(V^{A0})^{00}_{\mu\mu}+\sum\limits_{l\neq 0} H^{0l}_{\mu\mu}, & \mu=\nu,\quad \mu\in A \\ \sum\limits_{l} H^{0l}_{\mu\nu}, & \mu\neq\nu. \end{cases}$$

The Coulomb-interaction matrix is

$$C_{\mu\mu}=\sum_{B\in\text{LUC}}\ \sum_{\substack{l \\ (R^{0l}_{AB}\neq 0)}}\left[\sum_{\sigma\in B}\rho_{\sigma\sigma}(0)\left(\begin{array}{c|c} 00 & ll \\ \mu\mu & \sigma\sigma \end{array}\right)-Z_B(v^{Bl})^{00}_{\mu\mu}\right], \quad \mu\in A .$$

The matrix of one-electron Coulomb and exchange interactions is

$$A_{\mu\nu}=\begin{cases} \sum\limits_{\sigma,\eta\in A}\rho_{\sigma\eta}(0)\left[\left(\begin{array}{c|c} 00 & 00 \\ \mu\nu & \sigma\eta \end{array}\right)-\dfrac{1}{2}\left(\begin{array}{c|c} 00 & 00 \\ \mu\eta & \sigma\nu \end{array}\right)\right]+\dfrac{1}{2}\rho_{\mu\nu}(0)\left(\begin{array}{c|c} 00 & 00 \\ \mu\mu & \nu\nu \end{array}\right), & \mu,\nu\in A \\ 0, \quad \mu\in A,\quad \nu\in B,\quad A\neq B. \end{cases}$$

Finally, the crystalline sum of exchange interactions reads

$$G_{\mu\nu}=-\tfrac{1}{2}\sum_{l} P^{0l}_{\mu\nu}\left(\begin{array}{c|c} 00 & ll \\ \mu\mu & \nu\nu \end{array}\right) . \qquad (5)$$

In all the above equations $\left(\begin{smallmatrix}00\\ \mu\nu\end{smallmatrix}\middle|\begin{smallmatrix}ll\\ \lambda\sigma\end{smallmatrix}\right)$ are the crystalline sums of Coulomb and exchange integrals of $(\mu\nu|\lambda\sigma)$ type in the basis of atomic orbitals.[24] Inasmuch as the method of computing the Coulomb $C_{\mu\mu}$ and exchange $G_{\mu\nu}$ crystalline sums has been presented in detail in our previous works[25] we will drop any further discussion of this important point herein and will confine ourselves to only making certain comments while describing the results obtained.

Fock's matrix elements in the INDO approximation contain a series of semiempirical parameters[24] which are optimized following a method described previously.[26] Currently we use a system of parameters that make it possible to correctly describe the intramolecular and intermolecular interactions of the SiO_2 molecules, as well as the electronic structure of the various SiO_2 modifications.[21,22,26] We used that same system of parameters in earlier calculations of the STE structure in SiO_2 within the framework of the cluster model.[14] The AO basis incorporated the 3*s* and 3*p* AO of Si atoms and the 2*s*,2*p* AO of O atoms.

As we noted earlier, the LUC method presumes that the super unit cell used in the calculations is obtained through a symmetric extension of the crystalline unit cell. As a reasonable compromise between the LUC size and computation time for adiabatic potential-energy surfaces, we choose the ideal β-cristobalite structure whose unit cell contains six atoms (Si_2O_4). Its fourfold extension results in a Si_8O_{16} LUC. The lattice constant optimized in this model is 13.9 a.u., while the band structure agrees well with the results of other calculations and reproduces correctly the basic characteristics of the SiO_2 band structure. For example, the band gap of the crystal computed in this model by the restricted configurational interaction method is 8.1 eV, accounting for singlefold excited configurations. As shown below, on using the LUC method the mutual interaction of periodically disposed defects starts affecting the results in a significant way only when the next-nearest-neighboring defect pair is taken under consideration. Referring basically to the qualitative significance of the results obtained, we believe that on using the β-cristobalite as a prototype structure for a- and c-SiO_2 an adequate reproduction of features of current interest will result.

Computation of the electronic structure of the triplet excited state of the crystal was made by means of the UHF method. However, for exploring the possibility of radiative and nonradiative transitions in the ground (singlet) state of the crystal, calculation of the pertinent adiabatic energy surface is required. Comparing the results of both calculations is only justified within the framework of a unified method. Consequently, we also used the UHF method for calculating the electronic structure of the singlet state of the crystal. This requirement and the laborious computation of the crystalline sums of Coulomb and exchange interactions helps us to undersand why we had earlier confined our first study of that type to a relatively small LUC. To conclude, we note that the spin projection carried out in each calculation shows that the value of $\hat{S}^2$ in the triplet state fails to match 2 by only 0.002, making it possible to avoid using the extended-spin HF method.

All optical-absorption energies of defects listed below, as computed in the present work, were obtained as differences between calculated self-consistent total energies of the ground and excited states of the system (the ΔSCF method).

III. SIMULATION OF THE SELF-TRAPPING OF EXCITON AND HOLE

The advantage of our approach is that in the initial (ground) state of the system all sites of the cation and anion sublattices of the crystal are equivalent. This makes it possible to simulate to a certain degree of reliability the very initial stages of self-trapping. The difficulty in obtaining a perfectly definite result arises from the fact that the crystalline sums of nonlocal exchange interactions (5) will diverge if all elements of the density matrix $P_{\mu\nu}^{0l}$ (1) are to decrease too slowly with the distance, which immediately corresponds to the case of delocalized electron and hole (or to a metal). This phenomenon is of the same nature as the necessity of accounting for the nonsymmetric points $k \in \mathrm{BZ}$ when calculating the band structure of metals.[17] For that reason our approach has been to find displacements of the lattice atoms from their equilibrium positions, such as those which can lead to self-trapping of an exciton in a triplet state. Accordingly, we started from the presumption that these should apparently be oxygen displacements, as evidenced by an analysis of the experimental data, showing that Frenkel pairs are produced in the oxygen sublattice. It should be noted that our method allows starting from more general premises as well, which would, however, lead to a significant increase in the number of necessary computations in the particular case. As a matter of fact, even a small (about 0.1 Å) oxygen displacement perpendicular to the Si—O—Si bond is shown to be sufficient to bring about the significant localization of the hole onto that oxygen, while the electron localizes onto the two nearest-neighboring silicon atoms. Now, the best localization occurs in the case of oxygen displacements lengthening only one Si—O bond. Beginning with displacements of about 0.2 Å the spin density is already some 70% localized onto the three ions mentioned. This makes us confident in using Eqs. (1)–(5) for computing the adiabatic energy surface. To reduce the computational time, we minimized the total energy of the crystal in the triplet state only relative to the displacements of the O(1), O(2), Si(1), and Si(2) atoms, as shown in Fig. 1, fixing all other ions in their site positions. The singlet-state energy was calculated at the same values of the adiabatic coordinates as the triplet-state energy.

As mentioned above, the energy of the singlet-to-singlet lowest electronic excitation of the perfect crystal is 8.1 eV in our model. At the same time, the energy of the triplet excited state, corresponding to a 0.2-Å O(1) oxygen-ion displacement from the lattice site, is only by 5 eV higher than the ground-state energy of the crystal. The latter results from the Coulomb interaction of the hole, almost completely localized onto O(1), and the electron, some 45% of whose density is localized onto the Si(1) and Si(2) ions nearest to O(1). Further displacements of the O(1) ion into an interstitial position are accompanied by a relaxation of the immediate-neighborhood ions, only a small lengthening (about 0.046 Å) of the Si(1)—O(1) bond and an increase of the O(3)—Si—O(1) angle (by about 2°). In this respect the classical displacement trajectory of the O(1) ion from the lattice site to a new equilibrium position can conditionally be termed "rotation" around the O(3)—Si(1) bond. The last

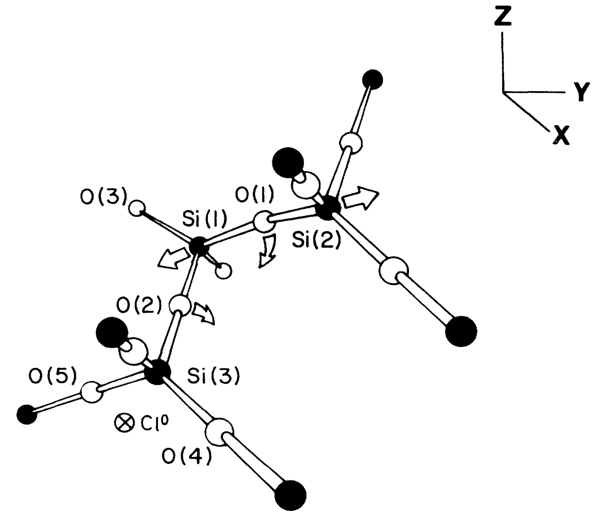

FIG. 1. Fragment of the ideal β-cristobalite structure. The arrows show the directions of the ion displacements taking place in triplet exciton self-trepanned and NNDP formation.

TABLE I. Magnitudes of ionic displacements from perfect lattice sites (Å) and energies at extrema points on the adiabatic surface of the crystalline triplet state relaitve to the perfect-crystal energy (eV).

	$Q_{O(1)}$	$Q_{O(2)}$	$Q_{\mathrm{Si}(1)}$	$Q_{\mathrm{Si}(2)}$	$Q_{O(4)}$	ΔE
STE	0.39	0.15	0.12	0.15		3.85
The top of this barrier between STE and NNDP	1.12	0.23	0.17	0.19		4.85
NNDP	1.73	0.38	0.25	0.34		1.35
NNNDP	2.39	1.49	0.34	0.36	0.45	0.21

statement agrees with the directions of the main nonacoustic normal modes obtained in Ref. 27 as a result of α- and β-cristobalite lattice-dynamics analysis. The displacements of the remaining relaxed ions are shown in Fig. 1. Ions Si(1) and Si(2) displace virtually perpendicular to the plane of the nearest oxygen ions, while O(2) displaces "against" O(1) with an insignificant lengthening of the Si(3)—O(2) bond (0.01 Å). The displacements of the ions from their lattice sites are shown in Table I. We note that the value of the O(1)-ion displacement agrees well with the one reported by us earlier[14] and also with Ref. 15. Lowering the energy of the system relative to the initial simulation point amounts to 1.15 eV. The atomic structure at the minimum is depicted in Fig. 2. The spin density is mainly localized in the region of the Si(1), Si(2), and O(1) ions, and constitutes, respectively, 0.21*e* and 0.23*e* at 3*s* AO of Si(1) and Si(2) and 0.95*e* at 2*p* AO of O(1). The remaining part of the spin density is delocalized over the neighboring silicon ions. The redistribution of the electron density is not that large: $-0.7e$ at O(1) and $-0.2e$ and $-0.16e$ at Si(1) and Si(2), respectively.

In this way, the hole counterpart of an exciton in our model proves to be almost completely localized onto a specific oxygen ion, displaced towards an interstitial position. The electron distributes more diffusely centered at the anion vacancy. For a comparison with experimentally observed characteristics, we turn now to the optical properties of this system.

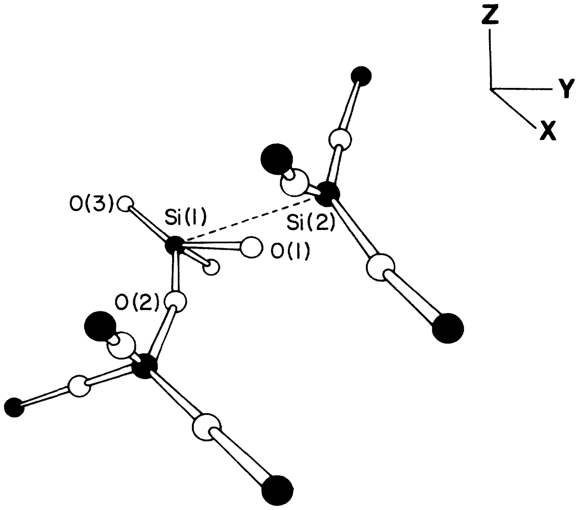

FIG. 2. Triplet STE model in $\mathrm{SiO_2}$.

The difference in total energy of the ground (singlet) state and the triplet state at the configuration corresponding to the energy minimum of the adiabatic potential energy surface amounts to 2.7 eV. This is "vertical-transition" energy from the triplet to the singlet term of the system which compares favorably with the peak position of the exciton luminescence [about 2.8 eV (Refs. 1, 3, 5, 7, and 9) in *c*-$\mathrm{SiO_2}$]. The diffuse distribution of the electronic component of the crystal excited state did not allow us to carry out any self-consistent calculations of its optical transitions. We believe, however, that the strongest STE absorption at 5.2 eV (Refs. 1, 3, 6, and 7) is due to the transition of its electron component. The electronic structure of the hole component is very near to that which can be attributed to the nonbridging oxygen hole center.[3] Here, two types of optical transitions are possible: electron transitions between O(1)-ion *p* orbitals, which are only partially allowed by the strong coupling of that ion to its surroundings, and transitions from quasilocal states in the valence band induced by the hole on the O(1) ion onto the empty *p* orbital of that ion. Our calculated transition energies of the former type are similar to each other and amount to about 0.6 eV. The quasilocal states have a diverse nature, and their wave functions spread over oxygen-ion orbitals of the nearest surroundings of Si(1) and Si(2) and of the displaced oxygen O(2) ion. The maximum value of the computed optical excitation energy from these states comprises 3.3 eV. There also is, however, a series of lower-energy transitions because of the presence of several quasilocal states. We consider it possible, ascribing the above-described series of optical transitions from the quasilocal states to the STE optical-absorption band in $\mathrm{SiO_2}$, which exhibits a peak in the range of 4.2 eV. The relatively low intensity of that band is explainable by the familiar[28,29] smallness of the oscillator strength of transitions from quasilocal states (see also Ref. 30), while its broadening to the red is due to transitions from a variety of quasilocal states. Based on the nature of the optical transitions described above, one can also easily understand why excitons are destroyed on optical excitation in the 4.2-eV band: finding itself in a quasilocal state, the hole does not self-trap (the way it does in alkali halides[30]), but starts migrating through the crystal, while the O(1) ion onto which the electron is passed returns to its starting position at the lattice site. In our opinion, the optical transition energy of 4.2 eV corresponds to the absorption peaked at 4.75 eV due to nonbridging oxygen atoms (NBOHC) in *a*-$\mathrm{SiO_2}$.[31,32] Similarly we attribute the 0.6-eV optical transition to the optical-absorption band of this center in the 2.0-eV range.[31,32] Both absorption bands are shifted to the red due to the small displacement of the O ion from its site and strong interaction with the surrounding ions.

To check the latter assumption, we computed the energy of optical transitions of the same nature as the 0.6- and 3.3-eV transitions but for larger O(1) displacements. Confirming our expectations, we get, e.g., 1.5 and 3.6 eV on displacing by 0.9 Å.

The above-described results appear, in our opinion, to provide solid arguments in favor of the conclusion that our obtained spatial and electronic structure of the triplet excited state of SiO_2 can be attributed to STE. As follows from our calculations, self-trapping results from the self-consistent effect of several factors. In a wide-gap dielectric with ionic-covalent character of the chemical bond, such as SiO_2, the ionic counterpart of the bond leads to a large crystalline field around the lattice sites, while the covalent counterpart of the bond determines the SiO_4 tetrahedral structure and the O—Si—O angles. At the anion lattice sites, the crystalline field creates a deep potential well for the electrons but also an opposite-sign potential for the holes. For that reason, oxygen displacement to an interstitial position creates favorable conditions for hole self-trapping thereon. On the other hand, the electron component of a quasifree exciton, being attracted additionally to the anion lattice site, undergoes a predominant localization therein. In strongly ionic oxides of cubic-lattice symmetry, this does not lead, however, to self-trapping (e.g., MgO and CaO). In the SiO_2 case, an essential role is played by the covalent component of the bond, determining both the lattice symmetry and the direction of the oxygen-ion displacements: the electron-excitation energy appears sufficient to weaken only one Si—O bond and displace the oxygen towards the octahedral empty space of the SiO_2 structure. The electron stimulates that displacement by localizing to substitute for the O ion in the crystalline field. The resulting energy gain by oxygen shift and electron localization constitutes about 70% of the total heat of self-trapping, while the remaining 30% comes from relaxation of the surrounding lattice. The decrease of the absolute values of the matrix elements of the crystalline field potential at the O(1) ion in its resulting position comprises about 10 eV, while the corresponding one at the Si(1) and Si(2) ions is about 3 eV, as compared to their normal site. The latter stimulates the self-trapping of the electronic and spin density in the region of these ions.

The natural question arises as to why should we not apply this kind of reasoning to hole self-trapping onto one of the oxygen ions, as suggested recently to model one of the paramagnetic centers in a-SiO_2.[33] The high efficiency of generating hole-trapped Ge centers in c-SiO_2 suggests that the holes are not self-trapped.[34] Studying this allows us to get a better idea about the role of the exciton electron in the process under consideration. The periodic model used by us makes it possible to consider only neutral unit cells. For clarifying this point, therefore, we have undertaken the following approach: It is known that atomic chlorine is a commonly occurring impurity in silicon dioxide[35] which incorporates in an interstitial position and remains paramagnetic. For that reason we added a chlorine atom to the LUC considered and found its equilibrium position in the lattice (see Fig. 1). Indeed, the Cl atom did remain neutral, while its separations from the O(4) and O(5) ions were equal to 1.47 and 1.53 Å, respectively. Further, we displaced the O(1) ion into a position, equilibrium for the STE case, and replanted its electron to the Cl atom. The energy of the electronic state obtained was higher by 5.6 eV than it was for Cl neutral. Computing the adiabatic potential of the system in that electronic state showed that the O(1) did not remain in an interstitial position but displaced backwards to the lattice site, the hole being delocalized over the anions, which are now equivalent. This result indicates that in the crystalline lattice considered, no hole self-trapping is possible onto any of the oxygen ions near its site. At the same time, in the exciton case the electron is localized in the region of the anion site, which does not let the anion return back to its starting position.

To conclude this section, we note that in the idealized β-cristobalite structure, displacements of the O(1) ion to both sides of the Si(1)—O(1) bond are equivalent. In the case of more complicated crystalline structures, and a-SiO_2, the differences in the local structure and the Coulomb field gradient of the whole lattice can lead to quantitative differences in the relaxational details of ions, as well as in the STE characteristics.

IV. STRUCTURE AND OPTICAL PROPERTIES OF DEFECTS

As it follows from the above-described results, the self-trapping of an exciton is accompanied by the weakening of the chemical bonding of the oxygen ion with one of the neighboring silicon ions and by only a small lengthening of the still tight chemical bond with the other silicon. For that reason it is difficult to expect that the occurrence of defects in this system on its transition into the second local minimum of the adiabatic surface in the excited state of the crystal will occur by way of breaking the latter bond. As a matter of fact, it appears that the most economical way from the viewpoint of energy losses is that in which the classical trajectory can be conditionally visualized as a further "rotation" of the O(1) ion around the Si(1)—O(3) bond. However, it too would require surmounting a barrier of about 1 eV. Displacements of the O(1), O(2), Si(1), and Si(2) ions from their equilibrium positions in the perfect lattice corresponding to the barrier top are presented in Table I. The directions of Si(1) and Si(2) displacements are virtually perpendicular to the planes of the nearest-neighboring oxygen ions (see Fig. 1). The O(2)-ion displacement goes as earlier against O(1) and is accompanied by a small lengthening (0.03 Å) of the Si—O(2) bond.

The defect pair configuration at which the adiabatic potential energy makes a second minimum is shown in Fig. 3, while the corresponding ionic displacements are presented in Table I. The large gain in energy at this configuration is due to the formation of an O(2)—O(1) chemical bond and to a strong redistribution of the electronic and spin densities within the defect region. In the

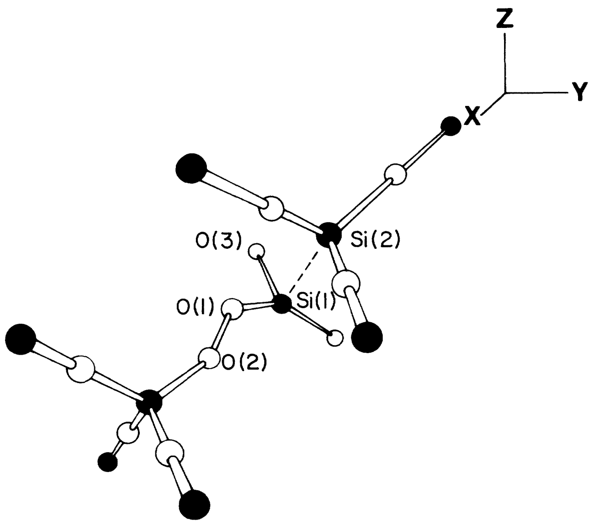

FIG. 3. Nearest-neighbor defect-pair model in SiO_2.

configurational-coordinate range described, we investigated three electronic states differing in multiplicity and in the character of localizing the spin density: a singlet and two triplets. We will briefly follow their basic trends as the system evolves from the STE configuration to the state, which we relate to a nearest defect pair. The moving force of this transition is the displacement of the O(1) oxygen and the formation of the O(1)—O(2) bond.

As the system approaches the configurational-coordinate point corresponding to the barrier, there is an increasing localization of the spin density over the O(1) and Si(2) ions (see Figs. 2 and 3). Near the barrier the distance between the adiabatic surfaces of the triplet and ground (singlet) states of the crystal decreases and two surfaces quasi-intersect in the second minimum in the barrier top region. On further increasing the displacement of the O(1) ion and relaxing the remaining ions, an increasing part of the electronic density, originally localized in the region of the O(1) and O(2) anions, is now redistributed in the region of the vacancy and localizes predominantly onto the Si(1) and Si(2) ions. There are three closely spaced adiabatic surfaces in the second-minimum range. The top one of these corresponds to a triplet state and a 75% localization of the spin density onto the O(1)-O(2) quasimolecule. The adiabatic surface of another triplet state is lower lying, virtually corresponding to the localization of the spin density onto the Si(1) and Si(2) ions. Energetically most favorable is the singlet state of the system, which differs from the triplet state only in the spin flip on one of the silicon atoms. The minima of the lowest triplet and singlet states of the system are virtually situated at the same configuration. The magnitude of the singlet-to-triplet splitting at various points on the adiabatic surface does not exceed 0.3 eV, while being about 0.01 eV at the minimum point. The difference in the electron density distribution in these states is rather insignificant.

The character of the lattice relaxation, as well as the distributions of electronic and spin density, tell that the above-described singlet and triplet states correspond to the formation of two weakly interacting E'-type centers at the same anion vacancy, as well as a center close in structure to the peroxide bridge. A comparison of the results of calculation with experimental results only for a-SiO_2 can be made, since no defect pair is produced by electronic excitation in α quartz. Furthermore no experiment can be carried out for SiO_2 of the β-cristobalite structure. We note, however, that the computational results of the optical-absorption energy of the system describe well the experimental optical-absorption spectra of the metastable defects produced by irradiation with an electron pulse at liquid-nitrogen temperature in a-SiO_2. According to the calculation, the transition, corresponding to the electronic excitation from $3s$ to $3p$ states localized onto the Si(2) ion, has an energy of 6.1 eV. The analogous excitation for the Si(1) ion requires 5.6 eV. Besides, we considered the charge-transfer transition from the Si(1) ion to the O(1)—O(2) bond. Its energy is 4.9 eV. Finally, an energy expense of about 1.7 eV is needed to excite the electron from bonding to nonbonding MO within the Si(1)—O(1)—O(2)—Si(3) bridge. The former two of the computed transitions agree well in nature and excitation energy with the familiar ones for the E' center in SiO_2 and correspond to the optical absorption of the so-called unstable E' centers in a-SiO_2 reported in Ref. 8. The spectrum obtained in Ref. 8 is strongly broadened to the red. One of the possible explanations could be the lower absorption energy of the Si(1) electron, perturbed by the nearly situated peroxide bridge, and still displaced charge-transfer transition. The latter explains also the possible reason for the occurrence of an exciton luminescence on optical excitation of the unstable E' centers in a-SiO_2 by a laser at a wavelength of 222 nm (5.88 eV).[8] As a matter of fact, the electron transfer from Si(1) to the nonbonding orbital at the Si(1)—O(1)—O(2)—Si(3) bridge leads to the breaking of the O(1)—O(2) bond and the restoration of the exciton configuration because of their Coulomb repulsion.

No optical absorption in the 1.7-eV range has yet been observed in pulsed experiments. The investigation of its kinetics could prove to be a method of evaluating the model discussed above. We presume that the defect pairs of this type are not produced in α-quartz because of the nonradiative transition.[36]

As follows from Table I, the second minimum on the adiabatic energy surface lies much lower than the one pertaining to the exciton. Qualitatively this agrees with the extremely slow-decay kinetics of the optical excitation of unstable E' centers reported in Ref. 8. The lack of any parallel increase in the optical absorption due to the metastable defects, accompanied by the destruction of the self-trapped exciton in a-SiO_2, tells of the possible recombination of the nearest pair of defects. We are not, however, inclined to reestimate the accuracy of the numerical values of the barrier heights of the direct and indirect transitions from the STE state to the NNDP state, as determined here. They can be overestimated due to both our failure to account for the electronic correlation and to the interaction of the periodically disposed defects.

An unusual feature of our model is the predicted possibility for the formation of two E' centers in the same anion vacancy. One of these, localized in the Si(2)-ion region, is similar in its structure and absorption to the E'_γ center. The second one corresponds to the proposed model of the unstable E'_α center.[3] As shown by our calculations, they perturb each other quite insignificantly and can be regarded as separated in the optical experiments. The last is confirmed also by similarity of E'-center characteristics in the bulk and on the surface[37] of SiO_2. At the same time, this model agrees quite well with the known ionicity of SiO_2, corresponding to an oxygen effective charge of $-1.2e$.[38,39] Both the ionicity and the displacement of Si ions make it possible to keep the electronic density in the oxygen vacancy the same as the oxygen effective charge. This corresponds to the charge- and spin-density distribution found presently and makes clear the meaning of the term "neutral oxygen vacancy."

The results under consideration are however, contradictory to the conclusion of previous works,[40–44] which predicted formation of a weak[40,43,45] or strong[41,44] Si—Si bond in the neutral oxygen vacancy in SiO_2. Direct comparison of our results with these works is impossible because of the difference in the approaches of the simulation of vacancy creation and the methods of calculation. In view of the results of the calculations of the electronic structures of β-cristobalite SiO_2 using the same approach as that employed in the present work,[22] we believe that the difference in the electronic and atomic structures of an oxygen vacancy obtained presently and previously[42,43] is due to the two following basic reasons. One is the consequence of consideration of the crystalline field in our approach [see (3)–(5)], which leads to substantially stronger ionic character of the chemical bond in the crystal,[22] compared with the molecular model employed in previous works.[44] Another basic difference lies in the methods of simulation and of vacancy formation. In our calculations a vacancy results from the displacement of an oxygen ion from a lattice site into an interstitial position and the consequent redistribution of electronic density in the crystal. In previous works[43,44] the vacancy "charge" and the electronic density distribution around a Si—Si bond were determined, assuming that the total charge of the molecular cluster including a vacancy is an integer. After creation of a nearest defect pair (Fig. 2), the ionicity of the chemical bond in the crystal obtained from our calculations leads to the effective charges of ions Si(1) and Si(2) to be about $1.8e$. These effective charges produces repulsion between Si(1) and Si(2), leading to the above-described relaxation and consequently creation of two E'-type centers in the single vacancy.

The problem still remains whether the defect pair comprising a peroxide bridge and the two E' centers located in a vacancy exhibit any EPR signal. Unfortunately, no experiment has been reported on a transient EPR signal at liquid-nitrogen temperature. Because of the spin-spin interaction between the two electrons in a vacancy, the defect pair is either singlet or triplet. The defect pair in the triplet state may exhibit an EPR signal similar to that of the E'' centers in quartz, as observed by Bossoli *et al.*[46]

Finally, we briefly discuss our results on the stimulation of further defect separation. In view of the smallness of the computed LUC's, they only bear a qualitative character and in fact effects of a strong defect interaction emerge. The equilibrium LUC structure obtained in the triplet state is shown in Fig. 4. Besides the displacements of the four ions considered earlier, the O(4)-oxygen displacement that bonds with O(2) also proves to be significant. The displacements obtained are presented in Table I. The O(1) ion displaces into a position close to the lattice site, occupied earlier by the O(2) ion. The latter appears in an interstitial position and has an effective charge close to zero. The equilibrium O(4)-O(2) separation is 1.38 Å, while the fragment Si(3)—O(4)—O(2)—Si(4) (see Fig. 4) is similar in spatial structure to the assumed structure of the small peroxide radical. The model and the possible origin of the latter in α-quartz have been discussed in Ref. 45. The justification for such a qualitative interpretation is also confirmed by the analysis of the spin-density distribution in the system. In the triplet state the spin density of $3s$ and $3p$ AO's on the Si(1) and Si(2) ions is about $0.7e$, while the one of the $2p$ AO of the O_2 ion is about $0.57e$. From this point of view, the structure of the system as a whole corresponds to two E'-like centers in the same anion vacancy and an interstitial oxygen atom, forming a bond with the anion of the regular lattice site (SPR). The optical absorption of the two E' centers computed here is similar and is at about 5.7 eV.

The transition barrier from the state corresponding to a nearest-neighbor defect pair in the state considered is about 0.8 eV. The absolute energy of the whole system proves to be only a little higher than the ground-state energy of the perfect crystal. This result is due to the strong interaction of the periodically distributed defects. Qualitatively it can be compared to the familiar effect of amorphication of c-SiO_2 as a result of continuing irradiation with dense electron beams[47] and also with heavy-ion tracks.[48]

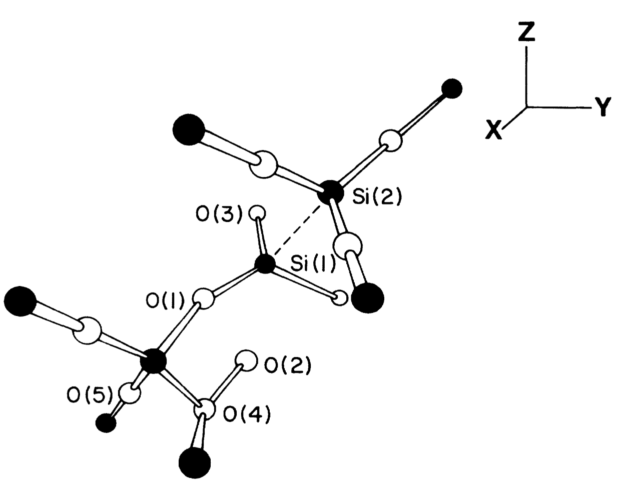

FIG. 4. Separated defect model in SiO_2.

V. DISCUSSION

In the present work, we have investigated the adiabatic surface for self-trapping of a triplet exciton and of a nearest defect pair in SiO_2 by applying the methods of the many-electron theory of defects to the exemplified structure of the ideal β-cristobalite.

As follows from the results obtained, the exciton self-trapping is conditioned both by the local structure of a small region of the sample (incorporating two SiO_4 tetrahedra) and the structure of the system as a whole. Comparison between the experimental STE characteristics of a-SiO_2 and c-SiO_2 shows that the magnitude of the exciton luminescent energy is most sensitive to structural changes, amounting to 2.8 eV in α-quartz and varying in time within the 2.1-eV range in a-SiO_2.[6,8] It is determined by the relative position of the adiabatic surfaces (AS) of the ground state of the triplet exciton and the singlet state of the crystal. As shown by our computational results, the triplet-exciton AS is rather flat in the range of the minimum. Thus, increasing the O(1) displacement from 0.39 to 0.51 Å leads to a decrease in energy of only about 0.08 eV. Lowering the singlet-state energy of the system on analogous displacements amounts to about 1 eV, which is explained by the rigidity of the Si—O bonds. In this way, small differences in the magnitudes of the ionic displacements, conditioned by the local structure of the specific center of self-trapping, can considerably change the relative position of the singlet and triplet terms. This possibility explains the difference in spectra and kinetics of the luminescence of a- and c-SiO_2.[6,8] At the same time we can expect that the qualitative characteristics of the exciton structure in various samples will be identical, which is confirmed by the lack of any differences in the optical-absorption spectra of STE in a- and c-SiO_2.

It is also natural to assume that the barrier height of the transition between the states corresponding to STE and NNDP may essentially depend on the specific short-range order structure of the sample. This will explain the possibility of the formation of NNDP in a-SiO_2 and its absence in c-SiO_2. Regrettably, we cannot discuss this point in greater detail here because of the lack of experimental data.

ACKNOWLEDGMENTS

The present research has been carried out under mutual agreement between Latvian State University and the Faculty of Science, Nagoya University. The authors thank the Ministry of Education, Latvian S.S.R. and the Faculty of Science, Nagoya University, for financial support. The present research is a part of the project of Research Information Center of National Research Institute for Fusion Science (NRIFS). Thanks are due to Y. Abe and T. Kawamura for their help in computational work and for providing us with an opportunity to use the Fujitsu FACOM-M-380 computer at the Computer Center of NRIFS. The authors would like to thank M. Georgiev for help and useful comments and N. Itoh, C. Itoh, W. B. Fowler, D. L. Griscom, W. Hayes, A. M. Stoneham, K. Tanimura, A. Trukhin, and R. Catlow for valuable discussions. Financial support by CSI Piemonte, by the Italian Ministero della Publica Istruzione (MPI), and by the Italian Consiglio Nazionale delle Ricerche (CNR) is gratefully acknowledged.

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