Structure of the Self-Trapped Exciton in Quartz

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We propose a structure for the self-trapped exciton in a-quartz on the basis of *ab initio* Hartree-Fock cluster calculations. It involves the displacement of a single oxygen atom in a direction nearly parallel to the hexagonal axis so that the shorter of its two silicon-oxygen bonds is lengthened. The energy and polarization of the recombination luminescence, the fine-structure parameters of the triplet state, and the magnitude and sign of the transient volume change induced by self-trapping are all correctly predicted. The calculations show no evidence for hole self-trapping in a similar geometry.

It has been known for many years that quartz, with a band gap of about 9 eV, nevertheless emits a broad luminescence in the blue when subjected to above-band-gap irradiation.[1] This blue emission has been decomposed into three components of which one, at 2.8 eV, is believed to be intrinsic;[2-4] it has been shown to be due to the decay of a triplet state with a lifetime of approximation 1 ms,[5,6] whose formation is correlated with a transient volume increase of the order of one SiO_2 molecular volume per center[6] and with two transient absorption lines at 4.2 and 5.2 eV.[6,7] Optically detected magnetic resonance has been performed on the triplet excited state[5] and it has been found that the principal fine-structure splitting is unusually large (22.6 GHz).

The triplet state was in the past tentatively assigned to a geometry in which two oxygen atoms approach to form a peroxy bond;[5,6] this was consistent with the large transient volume change associated with the center[6] and with the large fine structure in the triplet ground state of molecular oxygen.[8] Recently, however, semiempirical electronic structure calculations in the intermediate neglect of differential overlap approximation were reported in the cubic cristobalite structure[9] which suggested that many of the properties of the defect could be accounted for on the basis of the motion of a single oxygen atom, without a pronounced tendency for oxygen-oxygen bonding. The motion proposed was a rotation of an oxygen atom about one of the other silicon-oxygen bonds of a neighboring silicon atom. However, such a calculation cannot provide detailed predictions that can be compared with the experimental information available on the lower symmetry a-quartz structure; motivated by this, we here report all-electron Hartree-Fock calculations performed on two nine-atom clusters in the geometry of a-quartz.

Our calculations were carried out using the CADPAC electronic structure package,[10] which allows the user to surround the atoms treated quantum mechanically by an array of point charges to simulate the electric field of the crystal. The program can also calculate, without numerical differencing, the force due to the electronic state on each atom and can use this information to perform an efficient optimization of the geometry. We adopted two clusters of atoms of different shapes, both containing nine atoms: the first was centered on a silicon site of the perfect crystal and the second on an oxygen site. Diagrams of these clusters are shown in Fig. 1, in which the perfect-crystal geometries are dashed. The larger point-
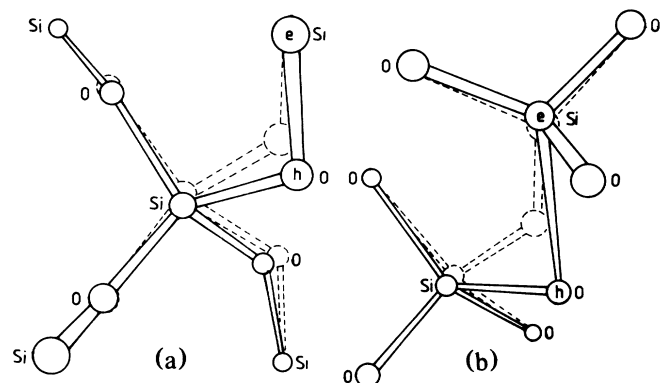

FIG. 1. View along the y axis of the clusters used in the calculations. (a) The silicon-centered cluster and (b) the oxygen-centered cluster. The perfect-crystal geometry is shown with dashed lines and the relaxed geometry of the triplet self-trapped exciton with solid lines. The atoms on which the electron and hole charge densities are primarily localized are indicated by the letters e and h, respectively.

ion clusters were obtained in each case by including all silicon atoms within 15.0 bohrs (7.9 Å) of the central atoms plus their four oxygen neighbors. For the purposes of assigning charges to the point-ion lattice and the quantum cluster, it was assumed that silicon atoms carried charge $+4$ and oxygen atoms charge -2. The only exceptions to this rule were oxygen atoms on the outer edge of the point-ion array, which were assigned a charge -1. This corresponds to a particular choice of boundary conditions for the cluster; our previous semiempirical calculations have shown no evidence of sensitive dependence of the results on the boundary conditions. Singlet energies were estimated by performing a closed-shell Hartree-Fock calculation and triplet energies by performing an open-shell calculation in which two of the one-electron states were singly occupied.

With the atoms in the perfect-crystal geometries, the excitation energies from the singlet ground state to the lowest triplet state were 7.4 and 13.3 eV for the Si-centered and O-centered clusters, respectively. The larger energy difference for the O-centered cluster arises because this cluster contains many fewer Si atoms and the confinement energy of the predominantly silicon-derived states at the bottom of the conduction band is therefore substantially increased. When the geometry of the Si-centered cluster was optimized in the singlet state subject to the restriction that it retain C_2 symmetry and with the requirement that the four outermost Si atoms remain fixed, a small relaxation of the atoms occurred. However, when the geometry of both clusters was optimized in the triplet state, with no restrictions on the symmetry, a much larger displacement of one of the oxygen atoms occurred. The energy gained relative to the perfect-crystal geometry in the triplet state was 3.5 eV for the Si-centered cluster and 5.6 eV for the O-centered cluster. This displacement lay predominantly along the hexagonal c axis of the crystal and for the particular oxygen atom chosen it lay in the negative direction (see Fig. 1); it tends to move the oxygen atom away from the silicon atom on the *short*-bonded side. The distortions in the neighboring atoms, where these were permitted to move, were small; the initial and final coordinates of the atoms in the clusters are shown in Table I. The similarity of the results from two clusters so different in their shape and their charge provides strong grounds for believing that they are not artifacts of the particular cluster shape and size employed, although calculations with larger clusters remain desirable. We have also checked for dependence of our results on the basis set used and on the size of ionicity of the point-ion arrays surrounding the clusters.

The hole component of the exciton was in each case strongly localized on the oxygen atom which undergoes the large displacement while the electron component was localized partly on this oxygen atom and partly on a neighboring silicon atom (see Fig. 1).

TABLE I. Positions of atoms before and after relaxation in the triplet state. All lengths in atomic units.

Atom	Coordinate	Perfect crystal	Si-centered relaxation	O-centered relaxation
O	x	2.590	2.263	2.059
	y	2.187	1.782	1.954
	z	1.226	0.512	-0.295
Si	x	4.317	4.568	4.446
	y	0.000	-0.249	-0.180
	z	0.000	-0.209	-0.184
Si	x	2.483	Not relaxed	2.500
	y	4.301	Not relaxed	4.457
	z	3.404	Not relaxed	3.574

We now compare the predictions of this optimized triplet geometry with the observed properties of the self-trapped exciton in quartz.

(1) The Stokes shift.—The Stokes shifts obtained for the self-trapping process are 74% and 89% of the perfect-crystal band gap for the Si- and O-centered clusters, respectively, compared with an experimental value of 69%.

(2) The radiative lifetime.—The observed lifetime of 1 ms is typical for a spin-forbidden transition of this energy and so will be correctly predicted by almost any model.

(3) The fine structure.—There are two principal sources for fine structure in nonmagnetic systems which are without rotational symmetry so that the orbital angular momentum is quenched:[11] The first is the spin-orbit coupling taken to second order in perturbation theory and the second is the magnetic dipole-dipole interaction between the spins of the carriers. We ascribe the fine structure in this case to the dipole-dipole interaction because the spin-orbit coupling is a rapidly increasing function of the atomic number and is small in oxygen; in addition, similar fine-structure parameters have been observed for an exciton in quartz trapped at a germanium impurity[12] whose atomic number is much larger. This would not be expected if spin-orbit coupling is important. The fine-structure tensor, therefore, has the following form (in S.I. units):

$$D_{ij} = \frac{1}{2} \frac{g^2 \mu_B^2 \mu_0}{4\pi} \langle \psi(1,2) | \frac{\delta_{ij} r^2 - 3r_i r_j}{r^5} | \psi(1,2) \rangle , \quad (1)$$

where $\psi(1,2)$ is the spatial part of the two-electron wave functions, μ_B is the Bohr magneton, and r is the displacement vector separating the two carriers. The expectation value is dominated by the amplitude for finding both carriers on the displaced oxygen atom, with a smaller correction term arising from the interaction between the hole on the oxygen and the electron on the neighboring silicon. These atoms are sufficiently distant that the detailed structure of the orbitals on the two atoms are unimportant.[11] The resulting fine-structure parameters

TABLE II. Fine-structure parameters from calculation and experiment.

	D (GHz)	E (GHz)	Principal axes	θ (deg)	ϕ (deg)
Observed	± 22.6	∓ 1.6	ρ	85	-35
			η	45	230
			ξ	45	60
Si-centered cluster	-40.8	9.8	ρ	81	-29
			η	34	254
			ξ	57	55
O-centered cluster	-18.1	3.0	ρ	85	-38
			η	174	-1
			ξ	86	52

TABLE III. Transient volume changes (in units of the SiO_2 molecular volume) from theory and experiment.

Calculated	
(1) Si-centered cluster, perfect crystal forces	$+1.55$
(2) Si-centered cluster, relaxed exciton forces	$+0.99$
(3) O-centered cluster, perfect crystal forces	$+2.08$
(4) O-centered cluster, relaxed exciton forces	$+1.18$
Experimental (Refs. 5 and 15)	About $+1.0$

from the calculation and from experiment are shown in Table II. The comparison is satisfactory for the major principal axis (the ρ axis), which dominates the observed splitting. The minor axes are also given quite well by the Si-centered calculation. We stress that in the model we propose the major principal axis is not associated with any interatomic direction, but instead arises from the anisotropic occupancy of the p orbitals on the displaced oxygen atom.

(4) The polarization of the luminescence.— When observed along a twofold axis of the crystal, the intrinsic component of the blue luminescence has been reported to possess a polarization parallel to the c axis of $+0.48$ (Ref. 3) and $+0.65$.[7] We can most simply estimate the expected polarization if we note that the transition is mostly a charge transfer of the electron component of the exciton from the silicon atom to the oxygen and the dipole vector is therefore proportional to the interatomic displacement vector. On this basis, we calculate the polarization to be $+0.44$ from the Si-centered cluster and $+0.65$ from the O-centered structure. We point out that a more exact calculation is not feasible since it would involve evaluating the dipole-matrix element between the singlet ground state and the singlet admixture introduced into the triplet state by the spin-orbit coupling.

(5) The transient volume change.— Since we have an electrically neutral defect, a detailed calculation of the volume change involving the effect of the long-range polarization field is not necessary[13] and a simpler formula[14] may be used, which expresses the volume change caused by the defect in the following form:

$$\Delta V = \sum_{i,j,k} s_{ijkk} G_{ij}, \qquad (2)$$

where s_{ijkl} is a component of the elastic compliance of the crystal[15] and G_{ij} is the force dipole or virial caused by the presence of the defect. We have calculated the virial by summing the difference between the forces on the nine atoms in the triplet state and the singlet state. In Table III we give the results for both the Si-centered and the O-centered clusters in the perfect-crystal

geometry and the self-trapped geometry; the consistency of the results for the different shapes of cluster and different geometries are an indication that this simpler theory is valid and the agreement with the experimentally observed number,[6,16] in which the uncertainty is rather large, is good.

(6) The excitation spectrum.— It is not possible to converge a self-consistent field calculation to an excited state if it has the same symmetry as the ground state. We therefore have to rely on one-electron energy differences to estimate the excitation energies of the relaxed triplet exciton. For the Si-centered cluster we find a one-electron excitation energy for the electron and hole components of 4.9 and 6.1 eV, respectively, while for the O-centered cluster these numbers are 7.3 and 5.7 eV. These results are in fair agreement with the observed peaks in the excitation spectrum at 4.2 and 5.2 eV,[6,7] although they do not allow us to distinguish which peak should be assigned to electron excitations and which to the hole.

We see that this model is capable of accounting for all the observed experimental features of the self-trapped exciton in α quartz with some degree of quantitative detail. We conclude by pointing out the difference of this model from the established picture of exciton self-trapping in the alkali halides[17] where the self-trapping of a hole is a principal driving force for the distortion; the binding of an electron serves only to increase the binding energy.[18] In quartz, we have been unable to find any geometry similar to those we have postulated for the exciton in which the hole is self-trapped, and this result is consistent with the conclusion of Hayes and Jenkin[19] that holes do not self-trap in crystalline quartz at temperatures down to 4 K. We suggest that localization by disorder may be important in producing the recently observed self-trapped holes in amorphous silica.[20] It seems that the role of the electron in quartz is crucial; the silicon-oxygen antibonding states in the conduction band make the self-trapping distortion, with its lengthening of a silicon-oxygen bond, very favorable in the presence of an electron.

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