Oxygen vacancy in α-quartz: A possible bi- and metastable defect

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Semiempirical cluster calculations are performed on positive (E'_1 center) and neutral oxygen-vacancy defects in α-quartz. A comparison is made of the various available Hamiltonians and the use of unrestricted wave functions. The results predict that these two defects form a bistable system, exhibiting the same two metastable configurations but differing in which configuration is lower in energy. The neutral charge state favors a configuration in which the silicon atoms adjacent to the vacancy relax only slightly away from their perfect crystal positions. The positive charge state yields a minimum energy configuration with large relaxation of the silicon on the long-bond side of the vacancy. This silicon atom, in fact, moves through its basal oxygen plane and bonds with an oxygen atom, making the oxygen atom threefold coordinated. Unpaired spin localization is consistent with experimental data from electron-paramagnetic-resonance studies on irradiated quartz.

I. INTRODUCTION

Electron-spin-resonance (ESR) studies in the 1960s of irradiated α-quartz suggested that oxygen vacancies might be significant defects in that material.[1-3] The E'_1 center is characterized by a spin-$\frac{1}{2}$ ESR signal associated with an sp^3 orbital on a silicon, pointing towards an oxygen site.[2] It was therefore natural to suggest that an oxygen vacancy is involved in this defect.

There were problems with this suggestion, however. A missing oxygen atom would leave behind two electrons on neighboring silicons, which presumably would interact to form either a singlet or a triplet state. And if the defect were negatively or positively charged, the observed spin localization on only one silicon would be difficult to explain, since one would expect substantial electron spin on both silicons adjacent to the vacancy.

In 1973, Feigl, Fowler, and Yip[4] suggested that the observed spin localization could take place for a positively charged vacancy if the electron-lattice coupling were such that a large, asymmetric atomic relaxation took place. Subsequent molecular-orbital calculations by Yip and Fowler[5] supported this notion. They envisioned a type of pseudo-Jahn-Teller effect associated with an odd-parity atomic displacement, and showed that significant electron localization could indeed result.

Yip and Fowler's calculations involved a modified extended Huckel approach. Several years later Rudra and Fowler[6] carried out similar calculations using a semiempirical quantum-chemical method,[7] modified intermediate neglect of differential overlap (MINDO/3), in its open-shell version.[8] In these calculations, the vacancy was simulated by an oxygen-centered atomic cluster consisting of eight silicon atoms, six oxygen atoms, and 18 terminating hydrogen atoms, with the latter included to avoid dangling bonds and associated spurious states. These calculations predicted that the positively charged vacancy would undergo a spontaneous asymmetric relax-

ation, with one silicon (the so-called "long-bond" silicon[9]) taking most of the positive charge and moving nearly into the plane of its three remaining oxygen neighbors. The unpaired spin would reside on the other silicon, which relaxed only a little.

Meanwhile, calculations[10] on other E'-type defects had suggested the possible importance of an oxygen atom in the quartz lattice which was not included in the above cluster but was "behind" the positively charged silicon. To investigate this in the case of the E'_1 center, Rudra and Fowler added that oxygen to the cluster in a simple way,[6] and it was found that the positive silicon would relax *through* the plane of oxygens and into the interstitial region, forming a bond with that back oxygen. This resulted in a threefold-coordinated oxygen, positively charged.[11]

Rudra and Fowler also showed that the neutral oxygen vacancy would be expected to undergo a small inward relaxation from the normal atomic positions, resulting in an equilibrium Si-Si separation of 2.5 Å and forming a singlet ground state.

Thus the relevant results of Rudra and Fowler[6] could be summarized as follows: The neutral oxygen vacancy resembles a slightly strained Si-Si bond, while the positive oxygen vacancy undergoes a spontaneous asymmetric relaxation with the long-bond Si moving to an interstitial location where it forms a back bond with an oxygen. In this case the positive charge is centered on that threefold-coordinated oxygen, and the spin is localized on the other silicon adjoining the oxygen vacancy.

Meanwhile, calculations of a totally different nature were being undertaken. Allan and Teter,[12] and Allan et al.[12] had been developing and carrying out electronic-structure calculations on silicon dioxide using density-functional theory in the local-density approximation. By the use of pseudopotentials and supercells, they managed to study the oxygen vacancy in different charge states.

The calculations of Allan et al.[12] were consistent with those of Rudra and Fowler[6] in that both predicted that

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the interstitial puckered configuration of the positively charged defect would be the most stable. The calculations differed, however, in one important way: Whereas Rudra and Fowler predicted that the asymmetric displacement would spontaneously occur, Allan *et al.* found a barrier between the puckered and the near-perfect-crystal (NPC) configurations. Furthermore, Allan *et al.* found that if they added an electron when the system was in the puckered configuration, the system would stay there; thus there was apparently a barrier to relaxation of the neutral vacancy from the puckered to the normal configuration.

The question of possible barriers in both charge states and the clear importance of oxygens outside the fundamental atomic cluster used by Rudra and Fowler motivated us to extend their calculations. We have done this by using a larger cluster and by investigating alternative semiempirical Hamiltonians.

II. CALCULATIONS

A. Preliminary notes

A logical extension of the atomic cluster used by Rudra and Fowler would have the following characteristics: (1) It would be oxygen-vacancy centered; (2) It would contain rings of atoms, including the back oxygen important in the relaxation of the positive silicon; (3) It would contain equal numbers of atoms on either side of the vacancy; (4) It would reflect the quartz structure.

With these properties in mind, we constructed the $Si_{14}O_{16}H_{26}$ cluster shown in Fig. 1. The geometry is defined in the usual way by "short" and "long" Si-O bonds, denoted by "SB" and "LB". The right-hand ring contains the oxygen atom (the back oxygen) which lies almost directly behind and along a Si-O vacancy axis. On each side there is a segment which is not part of the ring; this contains one of the second-neighbor silicons, along with H and OH terminators.

We then proceeded to carry out calculations on this cluster, in different charge states, using several semiempirical Hamiltonians. This was made feasible through
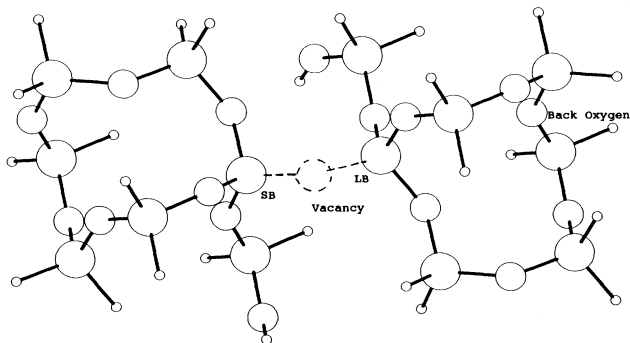
the acquisition of the computer code MOPAC 6.0, developed by Stewart.[13] MOPAC contains the MINDO, modified neglect of diatomic overlap[14] (MNDO), AM1 (Ref. 15), and PM3 (Ref. 11) Hamiltonians. (AM1 and PM3 are extensions of MNDO.) MOPAC also contains provisions for the determination of transition states and implementation of multielectron configuration interaction, along with other features not used in this study.

Stable geometries are predicted by minimizing the total cluster energy (electronic + nuclear) with respect to atomic position through a standard gradient minimization technique. Hydrogen terminators and their first neighbors are fixed to eliminate surface effect anomalies. Atomic charges were calculated using a gross population analysis checked against a Mulliken scheme. Calculations were run using both unrestricted (UHF) and restricted (RHF) Hartree-Fock Hamiltonians.

The semiempirical Hamiltonians differ in level of approximation and parametrization.[13] AM1 and PM3 use essentially the same approximations as MNDO except for a more sophisticated core-core repulsion term. PM3 is further extended by a more efficient parametrization technique, allowing a larger test set of molecules to be used. All three methods employ multipole expansions of electron-density distributions, which arise from products of atomic orbitals, in calculating two-electron two-center integrals. In marked contrast to this, MINDO two-electron two-center integrals depend only on atom type and interatomic distance. All integrals over atomic orbitals on two particular centers are set equal, so s and p orbitals do not make different contributions as in the other three methods. In addition, MINDO resonance integrals and core-core repulsion terms require diatomic parameters, while the others use only monatomic parameters. Diatomic parameters for the Si-O interaction are taken
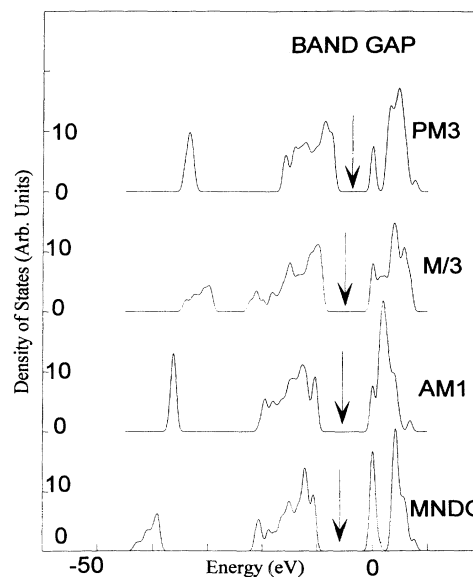

FIG. 1. Two-ring cluster ($Si_{14}O_{16}H_{26}$) representing α-quartz with an oxygen vacancy. Short-bond (SB) and long-bond (LB) directions adjacent to the vacancy are specified, as is the back oxygen which becomes threefold coordinated in the puckered configuration. Large circles are silicons, medium circles are oxygens, and small circles are hydrogens.

FIG. 2. Density of states for a perfect α-quartz cluster ($Si_{14}O_{17}H_{26}$) versus energy for each semiempirical Hamiltonian. Continuous curves are obtained by Gaussian broadening the one-electron eigenvalues. The center of the band gap is specified with an arrow.

from Edwards and Fowler[16] who optimized bond lengths and heats of formation for three Si-O containing molecules.

Before undertaking defect calculations it is prudent to check one's method against other results for the perfect crystal. The equilibrium geometry was chosen to have experimental α-quartz positions and we find that using these positions over those predicted by the method introduces only minimal strain in the cluster. The calculated electronic structure using any of the semiempirical Hamiltonians gives reasonable agreement with other calculations and with experiment. We find an SiO_2 band gap of about 9–10 eV and a density of states (Fig. 2) qualitatively similar to published results,[17] except that the lowest valence-band energies are too low due to excessively low energies for states containing mostly oxygen s orbitals. There is also a slight bias for charge to congregate near the center of the cluster due to termination effects, but this is not large and should cause no problems in comparisons of relative changes as the charge state is varied.

B. MINDO results

The E_1' center is calculated by removing the central oxygen from the cluster and adding a positive charge. In UHF and RHF formalisms we find both puckered and near-perfect-crystal (NPC) equilibrium geometries with the puckered being lower in energy by 0.1–0.2 eV. In the puckered configuration, shown in Fig. 3, the unpaired spin is found in the highest occupied molecular orbital (HOMO), which is comprised mainly of atomic orbitals from the SB silicon adjacent to the vacancy. More than half of the unpaired spin density is located on this silicon, and an additional 30% on its three oxygen neighbors. The two silicon next-near-neighbors (NNN) contained in the ring part of the cluster each hold 3.4% of the spin, while the nonring NNN has only 1%. This is consistent with previous arguments that associate the spin on the two NNN in the ring with experimentally observed weak hyperfine interactions.[6] The nonring NNN is inequivalent to the other two with respect to its orientation with the dangling bond on the SB silicon, and simple
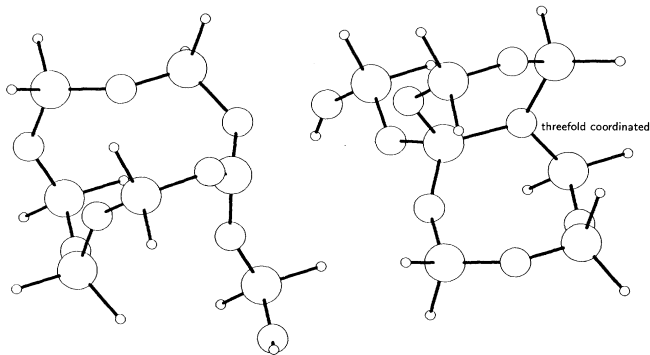

FIG. 3. Typical atomic positions for a puckered configuration geometry using the MINDO Hamiltonian. Note how the LB silicon has relaxed through the plane of its basal oxygens and bonded to a back oxygen. Large circles are silicons, medium circles are oxygens, and small circles are hydrogens.

tight-binding calculations predict the isotropic hyperfine interaction to be reduced for this nucleus.[20] Geometrically, the configuration is characterized by relaxation of the LB silicon through its basal oxygen plane to a puckered position in which it has formed a weak bond (2.07 Å) with a now effectively threefold-coordinated oxygen atom. The SB silicon also relaxes away from the vacancy, moving 0.05 Å toward the plane formed by its own basal oxygens. The +1 charge of the defect is localized completely on the puckered side ring of the cluster, the bulk of it trapped on the LB silicon. Some of this positive charge is also found on H terminators near the threefold-coordinated oxygen, but the oxygen ends up less positively charged than has been found in previous calculations.[6]

Although slightly higher in energy, the NPC configuration will be the geometry of choice for a small fraction of the time due to thermal effects. Again the unpaired spin occupies the HOMO, but this time the orbital contains a strong configuration from both SB and LB silicons. Most of the unpaired spin is on the SB silicon, but it is spread much more evenly than in the puckered case. The silicons have relaxed inward toward each other from their original 3.0-Å separation to an equilibrium position of 2.78 Å. The positive charge is distributed more evenly between the rings with about 52% on the long-bond side and 48% on the short-bond side. In both NPC and puckered configurations the uneven distribution of positive charge results in a dipole moment in the cluster when measured from an origin at the center of mass, which lies almost directly between SB and LB silicons. A small dipole (2.8D) is induced in the NPC configuration, oriented in the silicon-vacancy-silicon plane in a direction consistent with the positive charge being localized in dangling sp^3 orbitals on the silicons. The puckered configuration yields a large dipole moment (18.4D) that points directly from the SB side to the LB side, parallel to the LB silicon-back oxygen bond, showing that a substantial charge transfer has taken place in the formation of this configuration.

To characterize the thermal activity due to these two metastable configurations, we have calculated the total-energy barrier to relaxation between puckered and NPC positions. This was done by fixing the LB silicon at various positions along a line between its position in the respective wells, and allowing surrounding atoms to relax. The resulting energy diagram is shown in Fig. 4. Note that the puckered configuration is favored by about 0.2 eV and the barrier to relaxation from NPC to puckered is about 0.4 eV. The barrier position was also found using a more sophisticated saddle-point calculation, in which the difference vector between NPC and puckered configurations is systematically varied to zero with suitable constraints to ensure that the energy surface exhibits the appropriate behavior. This gave very nearly the same barrier configuration as our direct treatment. Simple thermal activation energy calculations suggest that at room temperature only the puckered configuration will be observed, and our puckered results are very consistent with experimental ESR data in quartz which clearly shows the unpaired spin to interact strongly with only
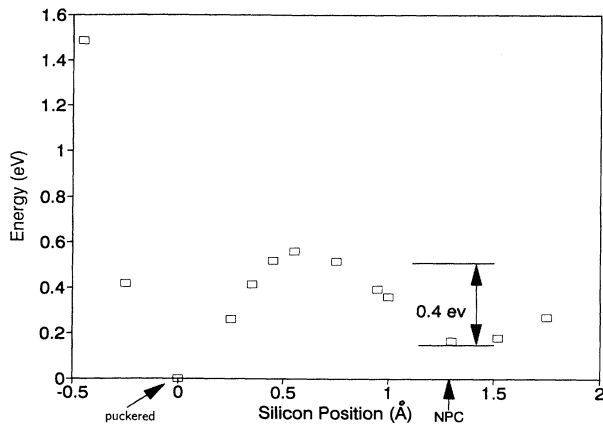
FIG. 4. Plot of total cluster energy for the E_1' center versus linear position of the LB silicon between its puckered and NPC locations, using the MINDO UHF Hamiltonian.

one silicon. It may be possible to create E_1' centers at low temperature such that a measurable number of NPC configurations are frozen in. These centers would be characterized by a hyperfine interaction between the unpaired spin and both silicons adjacent to the vacancy.

Calculations on systems containing unpaired spins can be performed UHF or RHF. In the UHF formalism α- and β-spin electrons in the same orbital are given different spatial dependences, removing their degeneracy. Spin densities result from the difference in population of the atomic orbitals representing the α and β electrons. In the RHF method the spatial dependence of opposite spin electrons associated with a particular eigenvalue is the same but unpaired spin can still be assigned from the population of atomic orbitals making up the HOMO. For MINDO E_1' calculations there is very good agreement between UHF and RHF. The other semiempirical methods exhibit significant differences between RHF and UHF results, suggesting that the MINDO treatment may be the most reliable for the system under consideration.

The precursor to the E_1' center is thought to be the neutral oxygen vacancy (NOV). To study this we have used the same cluster as before and created the oxygen vacancy at the same site. Again we find the existence of both a puckered and NPC minimum energy configuration. Looking at the electronic structure, we find the dipole moments to be qualitatively similar to those found for E_1' except that the puckered dipole is very much smaller (3.3D) for the neutral system. Analysis of the HOMO shows it to consist of s and p density on the silicons adjacent to the vacancy and their oxygen neighbors. The lowest unoccupied molecular orbital is antibonding, however, consisting of combinations of atomic orbitals on the same sites that minimize charge between the atoms. The bonding-antibonding splitting in this one electron treatment is 6.7 eV. This is consistent with the results of Rudra and Fowler.[6] The silicon-silicon NPC separation is 2.46 Å, closer by 0.3 Å to a normal silicon-silicon bond than in the positively charged case. This is reasonable because the silicons are sp^3 hy-

bridized and should form a near normal silicon-silicon bond, enlarged slightly by the added positive repulsions due to the polarizing effect of the three neighboring oxygens. The most salient difference, however, is that the NPC configuration is lower in energy than the puckered by 1.5 eV. Thus, the oxygen-vacancy defect in α quartz is predicted to be both bi- and metastable.

The energy barrier for the NOV depends on whether we do the calculation UHF or RHF, but in any case is on the order of tenths of an eV. For the above-mentioned UHF results the barrier turns out to be 0.5 eV and for RHF it is only 0.2 eV. Both methods predict the same energy near the NPC configuration, but in Fig. 5 we notice how much higher the RHF prediction becomes as the puckered configuration is approached. Also, we see that UHF puckered energies do not depend on multiplicity because the interacting unpaired spins are localized on silicons far apart from one another. We believe the RHF treatment to give less reliable energies when dealing with dangling bond unpaired spins concomitant with the puckered configuration, because RHF wave functions lack the variational flexibility to find the lowest-energy electronic structure. This is analogous to the well-known inadequacy of RHF treatments in predicting the dissociation energy of molecular hydrogen.[18] In the limit of large separations a UHF treatment correctly approaches the energetics of two isolated H atoms, while RHF still predicts a substantial interaction.

The probable mechanism for E_1' center formation is, firstly, the aforementioned creation of a NOV in the NPC configuration via some irradiation process. This defect will then trap a free hole and relax into the puckered configuration when sufficiently thermally activated. To test the energetics of this second step we look at the electrical level positions between the fully relaxed neutral and positive defects. This level is referenced to the experimental conduction-band minimum (0.9 eV below vacuum[19]) and is calculated from
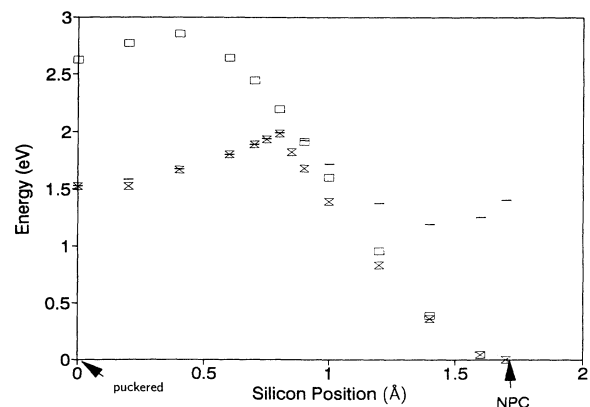
$$E(0/+) = E(0) - E(+) - E_{CBM}$$

FIG. 5. Plot of total cluster energy for the neutral oxygen vacancy versus linear position of the LB silicon between its puckered and NPC locations, using the MINDO Hamiltonian. Hourglass figures are for UHF, open rectangles are for RHF, and horizontal dashes are for UHF-triplet spin state.

where $E(0)$ is the total energy of the NOV in the fully re-laxed NPC configuration, $E(+)$ is the total energy of the E'_1 center in the fully relaxed puckered configuration, and $E_{CBM} = -0.9$ eV. The level is thus calculated to be $(0/+) = -4.89$ eV (meaning 4.89 eV below the conduction-band minimum) which puts it just below midgap.

C. Other results

PM3, AM1, and MNDO (all MNDO-based formal-isms) give results that in certain cases disagree consider-ably with each other and with MINDO. As mentioned above, the most important difference in these methods is in their parametrization, and all three are optimized to reproduce molecular properties. Therefore, the Si-O in-teraction arising out of atomic Si and O potentials (from the single-atom parameters) may not adequately carry over into a solid-state environment. With MINDO, how-ever, the Si-O interaction is represented directly via bi-centric parameters which have been thoroughly tested on silicon-dioxide-related systems by other investigators.[16] We therefore tend to have more confidence in MINDO results in these kinds of systems. Table I summarizes the energetics for the different Hamiltonians in the puckered configuration. The NPC energy is arbitrarily taken to be 0 and the puckered energy is listed relative to it.

The equilibrium geometries (puckered, NPC) are quali-tatively the same in all the methods. For UHF calcula-tions in PM3, the puckered E'_1 center is found to have a Si-back oxygen separation of 1.80 Å. This would seem to suggest a strong Si-O bond, but the puckered Si does not end up as positive as in MINDO. In fact, the positive charge is not as localized on the LB ring and the dipole moment is only 6.5D. Also, most of the unpaired spin ends up on the fourfold-coordinated puckered Si instead of the threefold-coordinated SB Si. These results are du-plicated in AM1 and MNDO. The NPC Si-Si separation is 2.98 Å in PM3 (2.72 Å in AM1 and 2.69 Å in MNDO), suggesting that there is little relaxation around the vacan-cy. It does not seem likely that the puckered configuration with this predicted electronic structure would exist, and it is inconsistent with known ESR data.[2] Both PM3 and AM1 predict the NPC configuration to be more stable than the puckered with this questionable electronic structure.

RHF E'_1 center calculations including spin density are found to be fairly consistent among all four methods.
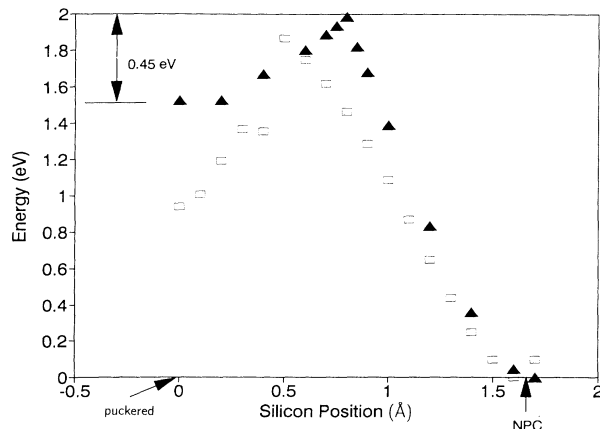

FIG. 6. Plot of total cluster energy for the neutral oxygen va-cancy versus linear position of the LB silicon between its puck-ered and NPC locations. Filled triangles are for MINDO UHF, open rectangles are for PM3 UHF.

The puckered configuration is always lowest in energy and the unpaired spin mostly localized on the SB silicon. The puckered silicon to threefold-coordinated oxygen bond length is between 1.80 and 1.91 Å, with the puck-ered silicon picking up most of the positive charge of the defect, while the oxygen becomes significantly positive only in PM3.

Results on the NOV are more consistent in that all methods agree that the NPC minimum is global, al-though MNDO predicts the two wells to be at nearly equal energies. The barrier to relaxation into the puck-ered configuration is 2 eV in both PM3 and MINDO, as shown in Fig. 6 and 1.6 eV for MNDO. There is very close agreement in most of the details of the NOV among MINDO, MNDO, and AM1. The NPC configuration predicts the SB and LB silicons to form a 2.4–2.5-Å bond with no spin localizations anywhere in the cluster. The puckered configuration resembles the result for the E'_1 center in that it gives a long puckered silicon to back oxy-gen bond length (> 2 Å) and spin does localize as a dan-gling bond on the SB silicon. Again, just as in the ques-tionable UHF puckered results, PM3 yields a puckered structure in which spin is localized on the fully coordi-nated LB silicon that has formed a bond (1.8 Å) with the threefold-coordinated back oxygen. In any case, this

TABLE I. Summary of equilibrium energies for puckered configurations of the neutral oxygen vacancy (NOV) and E'_1 center listed relative to the corresponding near-perfect-crystal (NPC) configuration, which is arbitrarily taken to be 0. UHF and RHF refer to cal-culations using unrestricted and restricted Hartree-Fock formalisms, respectively. All values are energies in electron volts. $(0/+)$ is an electrical level position, defined in the text.

	NOV				E'_1			
	PM3	AM1	MNDO	MINDO	PM3	AM1	MNDO	MINDO
UHF-puckered	0.96	0.66	0.06	1.52	0.21	0.51	−0.52	−0.17
UHF-$(0/+)$					−3.44	−6.55	−7.07	−4.89
RHF-puckered	1.99			2.58	−0.36	−1.23	−2.12	−0.09
RHF-$(0/+)$					−3.12			−5.01

configuration will not be observed due to the equilibrium energetics.

III. SUMMARY

The oxygen vacancy in α-quartz may be a bistable defect based on a consensus view of semiempirical quantum-chemical calculations. Figure 7 shows a configuration coordinate diagram of the defect in both charge states, displaying this bistability. A neutral vacancy would exhibit an equilibrium configuration in which only the silicon atoms adjacent to the vacancy site relax appreciably, forming a slightly soft Si-Si bond. This configuration can now trap a positive charge with attendant relaxation into what we have called the puckered configuration, forming an E'_1 center. The positive charge is trapped on atoms on the puckered-side Si-O ring, thus producing a sizable dipole moment oriented from NPC to puckered rings. The metastable nature of the defects may be observable in the case of the E'_1 center by some low-temperature production method, since the barrier between the two configurations is not particularly large.
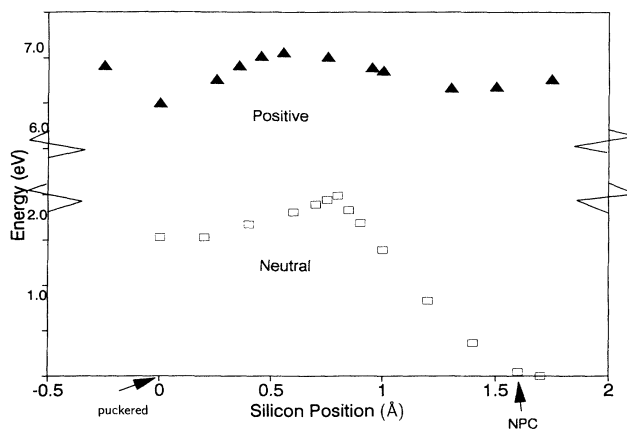

FIG. 7. Comparison of positive (E'_1 center) and neutral oxygen vacancy energy versus LB silicon positions between puckered and NPC configurations, using the MINDO Hamiltonian. Note the break in the energy scale.

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