

Many-electron treatment of the off-center substitutional O in Si

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We present, for the first time, a quantitative justification for the occurrence of a pseudo-Jahn-Teller effect at the neutral, isolated substitutional oxygen in Si, the origin of the well-known Si *A* center. We show that, in this case, multiplet effects must necessarily be taken into account. Our results also give values for the hyperfine interactions in the excited triplet state which are in excellent agreement with the experiment.

It is well known, since the pioneering experimental work of Corbett and Watkins,¹ that isolated substitutional oxygen in Si in both the neutral (O^0) and negative (O^-) charge states is found in off-center configurations with distortion axis along the $\langle 100 \rangle$ crystal direction. This is usually referred to as the "oxygen-vacancy pair" or Si *A* center, or even Si *B1* center.

It is established²⁻⁴ that oxygen introduces an orbital of a_1 symmetry lying deep in the gap and an orbital of t_2 symmetry energetically above. Therefore, for the negative charge state the ground-state electronic configuration ($\dots a_1^2 t_2^2$) yields a degenerate 2T_2 state and as such is Jahn-Teller (JT) unstable in the tetrahedral symmetry. In turn, for the neutral charge state the resulting configuration is $\dots a_1^2 t_2^0$, leading to a nondegenerate 1A_1 state; hence, it is not amenable to JT driving forces. The intriguing question thus remains as to what could lead the neutral system to a distorted lattice geometry as experimentally observed. Theoretical analyses^{5,6} on $Si:O_{Si}^0$ ascribe this to a vibronic coupling of the 1A_1 ground state with a close-lying 1T_2 excited state, thereby leading to a pseudo-JT (PJT) instability. Recent progress in this direction was achieved by DeLeo, Fowler, and Watkins.⁵ The authors studied this problem within the one-electron approximation, with the use of the hydrogen-terminated cluster model and utilizing the multiple scattering $X\alpha$ and linear combination of atomic orbitals—modified neglect of diatomic overlap (LCAO-MNDO) methods. Analyzing only the one-particle states obtained for the electronic structure of the 1A_1 lowest states, they found a possible coupling between the occupied a_1 and unoccupied t_2 orbitals and concluded that a PJT effect was responsible for the driving force for the distortion. A conclusive description, however, requires the analysis of the many-electron states, in particular, the explicit calculation of the many-electron 1A_1 and 1T_2 states and the role of correlation effects. In this Rapid Communication we show that a proper description of the $Si:O_{Si}^0$ system requires a higher degree of sophistication: The introduction of multiplet effects, which we include in a configuration-interaction (CI) procedure.

We adopt the cluster approach with the hydrogen-saturation boundary condition, and the electronic structure is obtained using the intermediate-neglect-of-differential-overlap (INDO) method.⁷ This method is a semiempirical self-consistent Hartree-Fock (SCF-HF) scheme based on LCAO expansion which includes one-center exchange integrals. The version used here, INDO/1-CI,⁸ is particularly suited for the description of closed-shell ground-state systems as well as for singlet and triplet excited states (via a CI

procedure).

DeLeo, Fowler, and Watkins⁵ show, within the MNDO cluster model, that the one-particle electronic structures obtained for the systems 1O16Si36H and 1O4Si12H are very similar. Because our results at the one-particle level agree closely with the MNDO results,⁵ we find it justified to base our discussions on the smaller cluster, which allows us to make use of sophisticated calculations.

The single-particle structure for the pure silicon cluster is calculated as

$$1a_1^2 1t_2^2 2a_1^2 2t_2^2 1e^4 1t_1^6 3t_2^6 3a_1^6 4t_2^0 .$$

The energy separation between the occupied $3t_2$ and lowest unoccupied $3a_1$ orbitals is calculated as 6.0 eV. A better estimate for the "band gap" is obtained through $\Delta E_a = \epsilon_a - \epsilon_i - J_a + 2K_a$, where J_a and K_a are the Coulomb and exchange integrals, respectively. In this case the result drops to 3.4 eV for the separation between the ground 1A_1 and lowest excited 1T_2 state. The valence-band width, as calculated by the difference between the $1a_1$ and $3t_2$ eigenvalues, is 13.6 eV, in fairly good agreement with the experimental result of 12.4 ± 0.6 eV.

When oxygen replaces the central silicon the orbitals relax, and a doubly occupied a_1 orbital appears in the band gap. The final calculated configuration is $\dots 3t_2^2 1e^4 1t_1^6 3a_1^2 4t_2^0 4a_1^0$. The $3a_1$ - $4t_2$ orbital separation is calculated as 3.5 eV, which is much too high an estimate for the 1A_1 - 1T_2 separation to serve as an argument for a PJT coupling. Similar results⁵ led to an investigation of the change of the character of the orbital functions associated with these two levels upon $\langle 100 \rangle$ distortion. However, this energy separation is considerably lowered in the CI treatment described below.

After the SCF calculation is performed on the 1A_1 reference ground state, all singlet configurations obtained with single excitations with the set $(3t_2, 1e, 1t_1, 3a_1 | 4t_2, 4a_1)$ are generated. This leads to 36 additional configurations, every one spin coupled to a pure spin state. The final singly excited CI (CIS) secular matrix is diagonalized, and every root now corresponds to a wave function which is a linear combination of these configurations. At this level of calculation the 1A_1 - 1T_2 separation is obtained as 1.4 eV, which is, perhaps, low enough to allow vibronic mixing. The calculated 1T_2 state is an essentially pure configuration, and the root of the CI is given basically by the diagonal value $\Delta E = \epsilon_a - \epsilon_i - J_a + 2K_a$.

We must also include correlation between the defect levels which would contribute the most to describe the multiplet effects. Thus double replacements CI among the $3a_1$

and $4t_2$ orbitals are considered on top of the single excitation CI just described, leading to six extra configurations: $a_1^0 t_x^2$, $a_1^0 t_x t_y$, $a_1^0 t_y^2$, $a_1^0 t_x t_z$, $a_1^0 t_y t_z$, and $a_1^0 t_z^2$. Again, these are coupled to pure spin states. The single- and double-CI (CISD) gives correlated ground and excited states. Every state is now a mixture of several configurations, and this is important because it allows us to determine (i) the effect of correlation on the 1A_1 - 1T_2 separation, which plays a decisive role in the PJT coupling, and (ii) the final admixture of states as expected for a PJT effect. As we shall see, upon distortion the 1A_1 state acquires a large contribution from the 1T_2 excited state (via the 1A_1 component of 1T_2).

We find that in the CISD calculation the energy of the 1A_1 ground state drops by 0.4 eV, while the excited 1T_2 is

$$\Psi_{1T_2(x)} = 0.81(\dots a_1^1 t_x^1) - 0.40(\dots t_x^1 t_y^1) + 0.30(\dots t_y^1 t_z^1) - 0.23(\dots t_x^2) + 0.13(\dots t_z^2) + \dots,$$

$$\Psi_{1T_2(y)} = 0.59(\dots a_1^1 t_y^1) + 0.55(\dots a_1^1 t_z^1) + 0.40(\dots t_y^2) - 0.35(\dots t_z^2) \\ + 0.20(\dots t_y^1 t_z^1) + 0.10(\dots t_x^1 t_y^1) + \dots,$$

$$\Psi_{1T_2(z)} = -0.59(\dots a_1^1 t_z^1) + 0.55(\dots a_1^1 t_y^1) - 0.36(\dots t_x^2) + 0.30(\dots t_z^2) \\ + 0.28(\dots t_y^1 t_z^2) - 0.15(\dots t_x^1 t_z^1) + 0.13(\dots t_x^1 t_y^1) + \dots,$$

while for the ground state it is

$$\Psi_{1A_1} = 0.94(\dots a_1^2) + 0.19(\dots t_x^2) + 0.19(\dots t_y^2) + 0.19(\dots t_z^2) + \dots,$$

where a_1 , t_x , t_y , and t_z stand for the defect levels $3a_1$ and $4t_2$. We clearly see that CI plays a central role, particularly for the excited 1T_2 state. The $\dots 3a_1^1 4t_2^1$ configuration, though dominant, contributes only $\sim 65\%$, the remaining 35% being distributed over excited configurations especially the doubly excited ones. For the ground state the dominant configuration contributes $\sim 88\%$. This explains the larger energy decrease obtained for the 1T_2 state as compared to the corresponding one for the 1A_1 state.

In hydrogen-terminated clusters the Si-H distance is, to a great extent, arbitrary. Most calculations, including ours, sets this distance to the Si-Si pure crystalline value of 2.35 Å. To assess the possible influence to the Si-H distance on our results, we performed calculations at variable Si-H distances; we find it does not affect our main conclusions. For instance, use of the suggested value of 2.12 Å (Ref. 5) leads to an increase of the 1A_1 - 1T_2 separation from 0.8–0.9 eV, and maintains the large configuration mixing as discussed above.

The Si:O_i^0 system should therefore be unstable at the T_d symmetry and couple to τ distortion modes. In Fig. 1 we show the splitting of the orbitals along the $\langle 100 \rangle$ distortion.⁵ This figure completely parallels the results of DeLeo, Fowler, and Watkins.⁵ In Fig. 2 we show the total energy variation obtained by the CISD calculations. The 1A_1 ground state is stable at 1.1 Å displacement of the O atom, in good agreement with previous results.⁴ The extent of configuration mixing is given by

$$\Psi_{1A_1} = 0.81(\dots a_1^2) + 0.58(\dots b_1^2) \\ + 0.11(\dots a_1^1 \bar{a}_1) + \dots,$$

where b_1 , b_2 , and \bar{a}_1 are the components of $4t_2$. We see

depressed by as much as 1.0 eV, leading to a final 1A_1 - 1T_2 separation of only 0.8 eV (Ref. 9). This small separation of the nondegenerate 1A_1 and the threefold-degenerate 1T_2 states may indeed allow vibronic mixing, and one then expects the ground state to be a combination. Therefore, we expect the off-center configuration to be describable indeed as a PJT effect. In other words, the contribution of multiplet splitting (obtained via correlation among the defect levels) acts to make the two many-electron states so close as to make the PJT effect operative.

The origin of the correlation contribution will now be traced in terms of configuration mixing. At the tetrahedral symmetry the calculated wave function for the different partners of the 1T_2 state are given by

now that the lowest 1A_1 state mixes with higher 1A_1 states even more. The excited many-electron states are split into the 1A_1 , 1B_1 , and 1B_2 components in C_{2v} symmetry, having their minima at ~ 1.0 Å. Opposite to a simple one-electron picture (Fig. 1), the lowest energy component of 1T_2 is found to be 1A_1 , followed by the 1B_1 and 1B_2 states. The energy for the 1A_1 - 1A_1 separation at 1.1 Å is calculated as 2.0 eV; i.e., the 1A_1 - 1T_2 separation increases by a factor of 2.5 upon distortion, as expected from a coupling of the

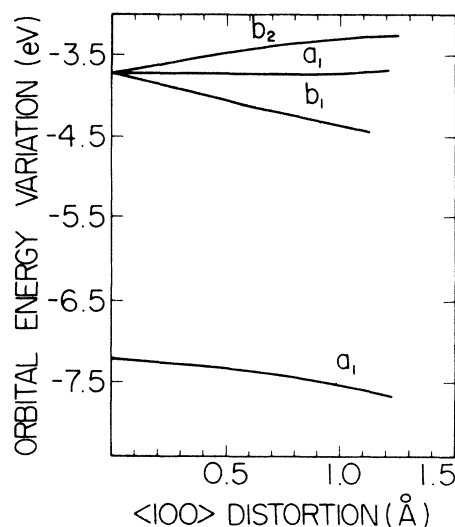


FIG. 1. Dependence of one-particle orbital energies with distortion for the a_1 and t_2 (\bar{a}_1, b_1, b_2) impurity levels.

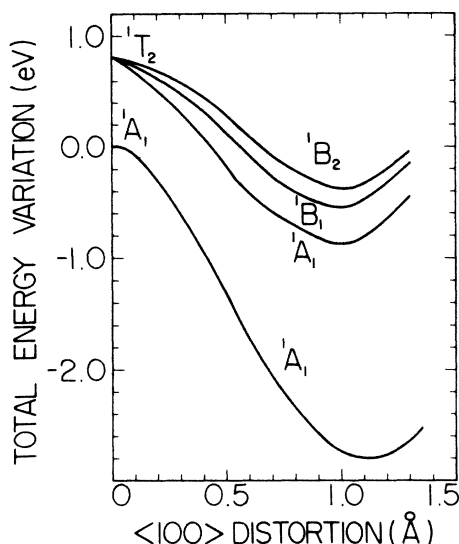


FIG. 2. Dependence on <100> distortion for the total energy of the neutral Si:O system in the ground state (1A_1) and the excited state $^1T_2(^1A_1, ^1B_1, ^1B_2)$. Results obtained from SCF-CI calculations including single and double excitations.

states. In the CIS representation this separation is roughly constant along the <100> distortion (the lowest energy component is again 1A_1). Comparing the results for the CIS and CISD models, we conclude that multiplet splitting has to be included to obtain repulsion of the levels along the <100> distortion. Analyzing the wave function, one sees that the lowest 1A_1 state has a large contribution of the 1A_1 component of the 1T_2 state, as one should expect. The correlated wave function for the 1A_1 component of 1T_2 calculated at 1.1 Å is

$$\Psi_{1A_1} = 0.88(\dots a_1 \bar{a}_1) + 0.33(\dots a_1^2) + 0.27(\dots b_1^2) - 0.19(\dots \bar{a}_1^2) + \dots$$

The $^1A_1-^1T_2$ separation obtained from the various models utilized here are summarized in the energy diagram of Fig. 3.

Based on the single-particle picture (Fig. 1) one may ex-

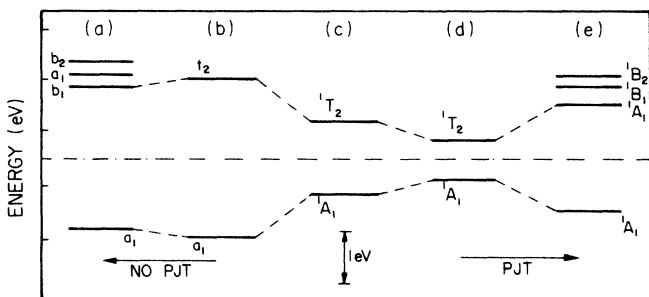


FIG. 3. Schematic $^1A_1-^1T_2$ separation energy: (a) one-electron model in C_{2v} symmetry, (b) one-electron model in T_d symmetry, (c) many-electron model with only single excitation in T_d symmetry, (d) many-electron model with single and double excitation in T_d symmetry, and (e) many-electron model with single and double excitation in C_{2v} symmetry.

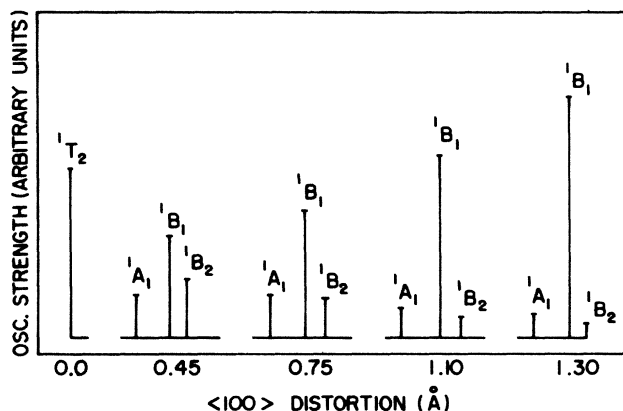


FIG. 4. Variation of relative oscillator strengths with <100> distortion for 1A_1 (ground state) \rightarrow $^1T_2(^1A_1, ^1B_1, ^1B_2)$ coupling.

pect the 1B_1 component to be lowest, rather than the 1A_1 , as calculated in the many-electron CIS and CISD models above. This limitation of the single-particle picture is found to be a consequence of the relaxation of the orbitals here and should already become apparent in separate SCF calculations for every state (Δ SCF model). Even simpler, the $^1A_1-^1B_1 < ^1B_2$ ordering is already obtained if one corrects for the Coulomb and exchange integrals, i.e., $\Delta E = \epsilon_a - \epsilon_l - J_{la} + 2K_{la}$. At this stage we found it of importance to consider the oscillator strengths for the transitions. We show in Fig. 4 the variation of the oscillator strengths (calculated in the dipole length form) for the CISD model along the <100> distortion. It shows that the $^1A_1-^1A_1$ intensity decreases, whereas the $^1A_1-^1B_1$ intensity increases along the distortion. At the off-center equilibrium configuration of 1.1 Å, the $^1A_1-^1B_1$ intensity is six times more intense than the lower $^1A_1-^1A_1$ transition. Thus, among the three components of the excited 1T_2 state the 1B_1 is the one more easily accessible by optical excitations.

Before concluding, we would like to comment on the EPR results of Brower¹⁰ for an excited triplet state of the Si:O⁰ center. Our calculations show that the lower-energy component of the 3T_2 state at the off-center configuration is the 3B_1 state with dominant $3a_14b_1(t_2)$ configuration. According to Brower, the excited triplet state exhibits hyperfine magnetic interactions over the two distant $^{29}\text{Si}^*$ neighbors and the ^{17}O atom. We calculate for the isotropic and anisotropic terms in the Si* atoms the values of $a = -69.3 \times 10^{-4} \text{ cm}^{-1}$ and $b = -9.8 \times 10^{-4} \text{ cm}^{-1}$, respectively. These are in very good agreement with the experimental values¹⁰ of $a = -51.24 \times 10^{-4} \text{ cm}^{-1}$ and $b = -20.79 \times 10^{-4} \text{ cm}^{-1}$. The hyperfine interaction over the oxygen atom is much smaller than over the silicon atoms. Our results show $|\psi(0)|^2 = 0.77 \times 10^{24} \text{ cm}^{-3}$ in excellent agreement with the value we extract from the data of Brower¹⁰: $|\psi(0)|^2 \approx 0.85 \times 10^{24} \text{ cm}^{-3}$. It is also important to mention that the charge distribution proposed by Brower for this triplet state is well reflected by our calculations. In summary, we may say that our results give the first quantitative justification for the occurrence of a pseudo-Jahn-Teller effect for the substitutional Si:O⁰ system. We conclude that multiplet effects give a dominant contribution to PJT coupling, in which coupling is evidenced by the repulsion of the involved levels with concomitant mixing of the orbitals upon

distortion.

We should comment, finally, upon the possible effects on increasing the size of the cluster. We can expect that the one-electron states will, as a whole, delocalize over the next shells of neighbors. This could bring a decrease in the energy separation between the one-electron impurity levels, which would favor configuration-mixing interactions. This effect would be counteracted, on the other hand, by a de-

crease of correlation effects; hence we estimate that the net effect would not fully alter the meaning of the conclusions of this work.

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