Electronic structure of E_1 centers in SiO₂[†]

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A linear combination of localized orbitals-molecular orbital (LCLO-MO) cluster method is applied to calculate the electronic structure of E_1 ' centers in the α -quartz structure of SiO₂. An O⁻ vacancy model, implying a net charge of |e|, is used. This corresponds to the F^+ center in simpler oxides. Calculations on the intrinsic E_1 ' center predict a highly asymmetric relaxation of the two silicons adjacent to the O⁻ vacancy. Detailed calculations of hyperfine parameters are carried out, and reasonable agreement with experiment is obtained. The asymmetric relaxation of the two silicons is an example of a pseudo-Jahn-Teller effect; parameters associated with this description are obtained and appear to be reasonable. Calculations on the extrinsic E_1 ' (Ge) center in SiO₂ also give satisfactory results.

I. INTRODUCTION

The generation of intrinsic and extrinsic paramagnetic defects in quartz and silica by irradiation with γ rays, x rays, and fast neutrons has been observed by electrical, spin-resonance, and opticalabsorption techniques. Typical examples of these defects in SiO₂ are the E'_1 center (intrinsic) and the *B* center (extrinsic). The E'_1 center involves an electron at an oxygen vacancy, ¹⁻⁷ and the *B* center is an electron trapped by a germanium atom substituted for a silicon atom.^{8,9}

The E'_1 center is one of the most important defect centers in SiO₂ because it is believed to be significant for detailed analysis of aging effects and radiation degradation within the silicon planar technology.¹⁰ It may also be the fundamental defect center in SiO₂. This center has been observed in both crystalline and glassy SiO₂,^{1,2} and has been found as a surface defect in SiO₂ powder.¹¹ Other versions of this center associated with chemical impurities are also observed, such as the E'_1 (Ge) center, which is an electron at a germanium atom substituted for a silicon atom in the E'_1 defect structure.⁵

The E'_1 center is characterized by an optical absorption peak² at about 6.2 eV and by an anisotropic electron paramagnetic resonance (EPR) spectrum.¹⁻³ The g tensor and hyperfine tensors deduced from the EPR data imply that the defect electron is in a nonbonding tetrahedral hybrid orbital on silicon and "pointing" in a direction normally associated with a Si-O bond.³

Many models for the E'_1 center have been proposed to explain its optical and paramagnetic properties. A summary of these models is given in Table I. From this table it appears that the single oxygen vacancy is more reasonable to use than others in interpreting some of the experimental data. However, the simple removal of an oxygen and an electron is not sufficient to explain the following

two basic properties of the E'_1 center.

(i) Since the silicons adjacent to the oxygen vacancy are nearly equivalent, it is expected that the unpaired electron should spend about equal time on both. However, the EPR data clearly indicate that the electron is localized predominantly in an (sp^3) orbital centered on a single silicon and oriented along a short-bond direction facing the oxygen vacancy.^{3,5}

(ii) The presence and directions of the two weak hyperfine interactions with two other Si atoms, as shown in the resonance data, cannot be fitted into the unrelaxed-lattice oxygen-vacancy model.³

Because of these two problems, this basic defect center has eluded firm identification. We have recently proposed a relaxed O⁻ vacancy model for the E'_1 center.¹² This model features a highly asymmetric relaxation of the two silicons adjacent to the oxygen vacancy. The present paper is a detailed theoretical investigation of that model. In Sec. II we present the results of linear-combination-oflocalized-orbitals-molecular-orbital (LCLO-MO) cluster calculations¹³⁻¹⁵ on the E'_1 center based on the relaxed O⁻ vacancy model. Section III contains a detailed analysis of the E'_1 -center hyperfine tensor based upon the wave functions obtained in Sec. II. In Sec. IV the asymmetric relaxation is analyzed by a pseudo-Jahn-Teller-effect model.¹⁶ Section V contains results of preliminary calculations on the E'_1 (Ge) center. In general, the theoretical results are consistent with the proposed model.

II. ATOMIC CONFIGURATION AND ELECTRONIC STATES OF E'_1 CENTER IN SiO₂

According to the relaxed O⁻ vacancy model for the E'_1 center in SiO₂, the asymmetric relaxation of the two Si atoms adjacent to the O⁻ vacancy is illustrated schematically in Fig. 1. The atomic labelings used in this figure are the same as those used in the previous paper.¹⁵ Figure 1(a) shows

11

Author	Model	Experimental evidence	Remark
Weeks and Nelson (Ref. 2) (1960)	an electron trapped at an unrelaxed O vacancy	optical absorp- tion and ESR	(a) it fails to explain the pres- ence of the strong hyperfine interactions
Silsbee (Ref. 3) (1961)	an electron is in a nonbonding <i>sp</i> ³ hybrid or- bital on an un- relaxed Si	strong hyperfine interaction of the electron with the ²⁹ Si nucleus	(b) it fails to explain the other two weak hyper- fine interactions
Castle <i>et</i> <i>al.</i> (Ref. 4) (1963)	an electron is trapped at a silicon which is located be- tween two oxy- gen vacancies	electron spin- lattice re- laxation	(b)
Feigl and Anderson (Ref. 5) (1970)	an electron is EPR (Ref. 5) in an sp^3 non- bonding directed orbital in an unrelaxed Si facing an oxygen vacancy		(c)
Ruffa (Ref. 6) (1970)	breaking of a Si–O bond	optical absorp- tion	(b)
Bennett and Roth (Ref. 7) (1971)	an electron is trapped by two displaced (pulled-together) silicons neighbor- ing an oxygen vacancy	optical absorp- tion	(b), (c) it also gives the wrong inten- sity of the hyper- fine interaction in the ESR spectrum

TABLE I. Models for the E'_1 center in SiO₂.

an unrelaxed-lattice oxygen vacancy and Fig. 1(b) shows the asymmetrically relaxed oxygen vacancy, in which the Si_0 atom is relaxed toward the $(O_{II})^-$ vacancy along the $Si_0 - O_{II}$ short-bond direction and the Si_{II} atom is relaxed away from the $(O_{II})^-$ vacancy along the $O_{II} - Si_{II}$ long-bond direction. This asymmetric relaxation of the silicons leads to a removal of the approximate degeneracy of the non-bonding hybrid orbitals which point toward the $(O_{II})^-$ vacancy, and a consequent localization of the electron in the orbital on Si_0 .

In the limit in which the two "halves" of the defect do not interact, one may treat each as an MX_3 molecule. It is then possible to show by stereochemical arguments that the half without the electron will tend to be planar with Si sp^2 hybridization, while the half with the electron will tend to be pyramidal^{12,17} with Si sp^3 hybridization. As the calculations presented below indicate, this appears to be a reasonable description of the actual situation. We have performed LCLO-MO calculations on the E'_1 center, using the Si₂O₆ cluster shown in Fig. 1 (Si_{VI} was not included). This approach has already been discussed in detail.^{14,15} We feel that the Si₂O₆ cluster is adequate for the following reasons: (a) It includes the important short-range forces and, through inclusion of Madelung-type potentials, the most important long-range forces as well. (b) The Si₂O₇ cluster from which this was obtained appears to treat adequately the valence states of SiO₂. While larger clusters could have been investigated, it would not have been feasible to map out the energy minima as functions of silicon positions with as much care because of computer costs.

The atomic positions in the cluster and the coordinate system have been given in a previous paper.¹⁵ The basis functions are those used previously: the localized Si(3s, 3p) and O(2s, 2p) orbitals. However, due to the oxygen vacancy in the E'_1 center, the following corrections to the matrix elements of the Fock operator have been taken into



FIG. 1. (a) Unrelaxed lattice oxygen vacancy in SiO_2 , presented as projections onto the plane defined by Si_0 , O_{II} , and Si_{II} . (b) Asymmetrically relaxed oxygen vacancy in SiO_2 , presented as projections onto the plane defined by Si_0 , O_{II} , and Si_{II} . (Atomic labelings same as used in Ref. 15.)

account in the calculation.

(i) The changes of atomic environment potential (U_a) at Si and at O sites are -0.6359 and -0.4033 Ry, respectively. These numbers result from the changes in the spherical parts of the point-ion and Coulomb potentials at the sites in question. The diagonal matrix elements of the Fock operator $\langle ai| F | ai \rangle$ are accordingly corrected by the same

amount, namely,

$$\langle ai | F | ai \rangle_{\text{corrected}} = \langle ai | F | ai \rangle_{\text{uncorrected}} + c$$
, (1)

where c is equal to -0.6359 and -0.4033 Ry for silicons and oxygens, respectively.

(ii) The corresponding corrections for the oneelectron energy parameters ϵ_{ai} are

 $\epsilon_{ai \text{ corrected}} = \langle ai | F | ai \rangle_{\text{corrected}} \pm \langle ai | U_{a \text{ corrected}} | ai \rangle,$ (2)
where the plus sign stands for oxygens and the

minus for silicons. The matrix elements $\langle ai | U_{a \text{ corrected}} | ai \rangle$ can be evaluated by assuming that $\langle ai | U_{a} | ai \rangle$ is directly proportional to U_{a} at the atomic site in question.

By allowing Si_0 and Si_{II} to relax along the bond directions as indicated above [Fig. 1(b)], the total system energy can be minimized. The atomic positions of the two Si atoms which correspond to minimum energy are

$$Si_0(0.1492, 0.0252, 0.0664),$$

$$Si_{II}(5.1664, -0.7401, 4.0038)$$
 bohr.

indicating for Si₀ a relaxation of 5.48% of the Si₀-O_{II} distance toward the vacancy and for Si_{II} a 27.4% relaxation away from the vacancy. This highly asymmetric relaxation of the two silicons is consistent with the relaxed O⁻-vacancy model. The shape of the energy-vs-displacement curve is discussed in Sec. IV.

The calculated energy levels for the Si₂O₆ cluster corresponding to the minimum total system energy are shown in Fig. 2, and the calculated wave function for the E'_1 unpaired electron ψ (E'_1) is given by

$$\begin{split} \psi(E_1') = 0.5408\varphi_{\text{Si}_03s} + 0.7900\varphi_{\text{Si}_03p_x} + 0.1219\varphi_{\text{Si}_03p_y} + 0.3383\varphi_{\text{Si}_03p_z} + 0.0430\varphi_{\text{Si}_{\text{II}3s}} - 0.1341\varphi_{\text{Si}_{\text{II}3p_x}} \\ + 0.0769\varphi_{\text{Si}_{\text{II}3p_y}} - 0.1622\varphi_{\text{Si}_{\text{II}3p_z}} + \text{other terms for oxygen atoms ,} \end{split}$$

in which $\psi(E'_1)$ is expressed as a linear combination of LO's centered on the two silicon atoms and on the six oxygen atoms.

Some important results for the E'_1 center can be deduced from the wave function $\psi(E'_1)$.

(a) A Mulliken population analysis for this wave function indicates that the electron density distribution in $\psi(E'_1)$ is $\operatorname{Si}_0(3s^{0*22}3p^{0*60})\operatorname{Si}_{II}(3s^{0*01}3p^{0*08})$. In other words, the unpaired electron spends 82% of its time on Si_0 compared with 8.5% on Si_{II} .

(b) As the electron is more strongly associated with Si₀, it is in an orbital of 22% atomic 3s character and 60% atomic 3p character. This implies that the electron is in a nonbonding sp^{2*7} hybrid orbital on Si₀, as compared with the ideal tetrahedral sp^3 hybrid orbital.

(c) The coefficients of the wave function on Si_0 indicate that the $sp^{2\cdot7}$ hybrid orbital is oriented almost along the $\text{Si}_0 \rightarrow O_{II}$ short-bond direction (less than 2° from the $\text{Si}_0 \rightarrow O_{II}$ direction).

All these results clearly indicate that the E'_1 defect electron is strongly localized in an approximately sp^3 hybrid orbital centered on Si₀ oriented almost along the Si₀ \rightarrow O_{II} short-bond direction. This situation is consistent with the observed strong hyperfine interaction and anisotropic *g*-tensor data.^{3,5} Further details of the hyperfine tensor analysis are given in Sec. III.

Several other remarks about our E'_1 -center calculations are appropriate.

(i) The calculated Wolfsberg-Helmholtz parameters (0.57 - 0.85) between the two silicons are

(3)

(4)

- 55





Si206

Si3p

FIG. 2. MO energy-level diagram for Si_2O_6 and $GeSiO_6$ clusters. Shown are the doubly occupied states, analogous to the valence bands in the perfect crystal, and the singly occupied state associated with the ground state of the center.

considerably smaller than the value of 1.75 which is used most often in extended Hückel calculations.¹⁸ In other words, the Hamiltonian matrix elements between the two silicons in this calculation are correspondingly weaker than those in the extended Hückel calculation. Probably it is this weakness which allows the asymmetric relaxation in the E'_1 center, in that it tends to uncouple the two "halves" of the defect.

(ii) The EPR experiments are consistent with only one energy minimum associated with the asymmetric relaxation, as described above, on which our calculations have been based. Accordingly, the secondary energy minimum associated with the opposite direction of relaxation will presumably be higher than the first one. The energy difference between these two minima might be obtained by an optical-absorption technique. However, our calculations are not accurate enough to predict such a fine difference (in our calculations, the secondary energy minimum for the opposite relaxation is actually 0.081 eV *lower* than the minimum which we investigated).

(iii) The calculations also showed that in an O^{2-} center the two silicon atoms prefer to relax away from the oxygen vacancy along the two Si-O bond directions. More specifically, the Si₀ relaxes away from the O_{II} vacancy along the O_{II} - Si₀ direction by 32.8% of the normal Si₀-O₁₁ bond distance,

and the Si_{II} relaxes away from the vacancy by 32.5%. In other words, Si₀ and Si_{II} relax into the planes defined by their three neighboring oxygens, respectively. This situation is consistent with stereochemical arguments and is also consistent with the theoretical results of Bennett and Roth.⁷

(iv) From the MO energy-level diagram (Fig. 2) for the E'_1 center, an optical transition from the valence band to the single occupied level at 9.2 eV is predicted. An empty defect level lies 8.9 eV above the singly occupied level. These transition energies are larger than the experimental value² (~6.2 eV), which could be due to either of these. The disagreement is probably due to spurious surface effects and the neglect of d orbitals in the calculations. It has been shown by Bennett and Roth⁷ that the conduction-band levels would be shifted down considerably by the inclusion of d orbitals in their calculations, and presumably the defect levels would also be shifted downward.

III. HYPERFINE TENSOR OF E'_1 CENTER IN SiO₂

The success or failure of any model of the E'_1 center must rest on whether it can lead to the observed hyperfine data. For this reason we have carried out a detailed calculation of the weak hyperfine components, based upon the relaxed O⁻ vacancy model.

The direct magnetic interaction of an electron with a nucleus consists of two parts. One is the isotropic Fermi contact interaction, characterized by a quantity A defined by³

$$A = \frac{8}{3} \pi g_e \mu_B g_N \mu_N |\psi(0)|^2, \tag{5}$$

which contains both electron (e) and nuclear (N) g factors and Bohr magnetons. $|\psi(0)|^2$ is the wave function density at the nucleus. In units¹⁹ consistent with those of published E'_1 -center data,³

$$|g_e \mu_B g_N \mu_N| = 5.239 \times 10^{-28} \text{ cm}^2$$
 (6)

for ²⁹Si.

The second part of the interaction is the anisotropic dipole-dipole interaction¹⁹ between the nucleus and an electron at position \vec{r} with respect to the nucleus:

$$\widehat{\mathcal{H}}_{dipolar} = -g_e \mu_B g_N \mu_N \left(\frac{\widehat{S} \cdot \widehat{I}}{r^3} - \frac{3(\widehat{S} \cdot \overrightarrow{r})(\widehat{I} \cdot \overrightarrow{r})}{r^5} \right) , \quad (7)$$

where \hat{S} is the electron spin and \hat{I} the nuclear spin. It is convenient to write $\hat{\mathcal{K}}_{dipolar}$ in terms of the anisotropic hyperfine tensor T, defined by the equation

$$\widehat{\mathscr{H}}_{dipolar} = h\widehat{S} \cdot \overline{T} \cdot \widehat{I} .$$
(8)

The components of \overline{T} are obtained by taking expectation values $\langle \cdots \rangle$ with respect to the wave function. They are elements of the following matrix:

$$[T] = \frac{-g_e \mu_B g_N \mu_N}{h} \left(\begin{pmatrix} \frac{r^2 - 3x^2}{r^5} \\ -\left\langle \frac{3xy}{r^5} \right\rangle - \left\langle \frac{3xy}{r^5} \right\rangle \\ -\left\langle \frac{3xy}{r^5} \right\rangle & \left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle - \left\langle \frac{3yz}{r^5} \right\rangle \\ -\left\langle \frac{3xz}{r^5} \right\rangle & -\left\langle \frac{3yz}{r^5} \right\rangle \end{pmatrix} \right)$$
(9)

By evaluating the elements of [T] and diagonalizing the matrix, one obtains three solutions. These correspond to principal directions of [T]. Experimentally, for the E'_1 center, two of the resulting diagonal elements are equal (this is referred to as axial symmetry). The third element may be called the *major principal value*; the direction associated with it is the major axis of the hyperfine tensor. The major principal value of $\hat{\mathcal{K}}_{dipolar}$ is one-fourth of the quantity³ B_{\parallel} ; B_{\parallel} in turn is *h* times the major principal value of [T].

Both A and B_{\parallel} , as well as the major axis, have been determined experimentally by Silsbee for one strong and for two weak ²⁹Si interactions; thus a quantitative comparison with theory is possible. The short-range nature of the magnetic interactions allows some qualitative observations as well. The results of Sec. II indicate that the strong hyperfine interaction of the E'_1 center is consistent with one result of the present calculation, namely, a strong localization of the unpaired electron on Si₀ in a nearly sp^3 orbital pointing toward the oxygen vacancy. There are two limiting cases in which analysis of the weak hyperfine interactions due to other silicons would be made as easily.

(a) If the electron were totally localized on Si_0 , so that the coefficients of orbitals centered on other silicons were zero, then the isotropic part of the weak hyperfine interaction would be very small, since this is a measure of wave-function density at a neighboring silicon site. Furthermore, the major axis of the anisotropic part would be approximately the vector connecting the nucleus with the most probable position of the unpaired electron.^{3,12}

(b) If the wave function density on neighboring silicons were moderately large, it would be this part of the wave function which would determine the hyperfine tensor, and the larger component on Si_0 could be neglected. This approximation has been used in the analysis of defects in silicon by Watkins and Corbett.²⁰

Because it was not obvious that our result fell into either of these categories, detailed calculations of the hyperfine tensor were made. These calculations followed the procedure outlined above and are somewhat similar to those performed on the $V_{\rm K}$ center by Daly and Mieher.²¹ We did not, however, include any exchange polarization effects.

In the LCLO-MO calculations we have included

only valence orbitals. However, because the hyperfine parameters are sensitive to details of the wave function near the nucleus in question, it is important that the wave function be Gram-Schmidtorthogonalized to the core states on that nucleus. We have neglected all wave-function components centered on oxygens because of their small coefficients and small amplitudes near the Si nuclei. Hence the E'_1 -center wave function which we have used in calculations involving Si_{II} is of the form of Eq. (4), without the oxygen terms, but with some core-state amplitude due to orthogonalization. In investigating hyperfine interactions due to silicons which were not in our LCLO-MO calculation, we started with the large amplitudes on Si_0 and orthogonalized to both core and valence states of the other silicon.

The execution of this rather straightforward calculation is somewhat lengthy. Aside from wavefunction overlap-integrals arising from the orthogonalization, there are three types of matrix elements to be evaluated: one-center (both wavefunction components on the silicon) and two twocenter [both components on the other silicon (Si₀), and one on each silicon]. Considerable algebra is involved with the angular parts of these integrals, but all of the two-center integrals were evaluated numerically using Löwdin's α -function technique.^{22,23} The entire numerical procedure was carried out by our program HYPER on the CDC 6400 at Lehigh University.

Several quantities were varied from one calculation to the next. These included the atomic positions and the atomic wave functions used to form the molecular orbitals. Some results of these calculations are shown in Tables II and III. Before discussing the comparison between theory and experiment, one should note comparisons between different theoretical results; e.g., columns (a), (c), and (e) of Table II involve calculations performed with different atomic functions. It can be seen that the theoretical value of the anisotropic hyperfine constant increases by a factor of 3 in going from Huzinaga²⁴ to Clementi's²⁵ atomic functions (calculated for ${}^{1}S$). This is noteworthy, inasmuch as these functions represent atomic calculations of comparable quality.

Thus one is forced to conclude that there is at present a basic limitation in the accuracy of our calculations, as large as a factor of 3, originating from uncertainties in the atomic calculations from which the wave functions are obtained. This sensitivity to the functions is not surprising, inasmuch as the hyperfine interaction varies rapidly with distance. Consequently, apparently small changes in wave functions can lead to large changes in hyperfine parameters. Because this is the case, we must view "agreement" between theory and experi-

		Yip, Fowler		Huzinaga		Clementi
	Experimental ^b	(c)	(d)	(e)	(f)	(g)
Isotropic hyperfine constant A (in 10^{-4} cm ⁻¹)	7.94	5.72	1.44	12,9	4.91	11.7
Anisotropic hyperfine constant B_{II} (in 10 ⁻⁴ cm ⁻¹)	1.21	3.70	1.82	1.56	1.00	4.84
Direction of ^a major axis of hyperfine tensor	28.3°	13.4°	17.5°	11.5°	11.7°	14.0°
Ratio of isotropic to anisotropic con- stants	6.6	1.5	0.79	8,3	4.9	2.4

TABLE II. Experimental and calculated hyperfine parameters for the E_1^\prime center (weak $^{29}\mathrm{Si}_{11}$ interaction).

^aComputed from the hyperfine parameters of Ref. 3.

^bWith respect to Si_0 -Si_{II} axis.

 e Wave functions from Ref. 15; only Si₀ and Si_{II} displaced from normal, as in text [Eq. (3)].

^dSame as (c) plus a particular motion of O_{VI} by 0.44 Å.

^eWave functions from Ref. 24; only Si_0 and Si_{II} displaced as in (c).

 ${}^{\mathbf{f}}\mathbf{S}ame$ as (e) plus motion of $O_{\mathbf{VI}}$ as in (d).

^gWave functions from Ref. 25; only Si_0 and Si_{II} displaced as in (c).

ment somewhat carefully. It is our assessment, in fact, that order-of-magnitude agreement is all that one can expect.

Given this criterion, we argue that the agreement between theory and experiment indicated in Table II is satisfactory. Magnitudes of isotropic and anisotropic constants, and their ratio, may be computed to within 40% agreement with experiment. There is a fairly consistent disagreement with angles, of order 10° . There are several possible reasons for this. (a) Perhaps Si_0 moves toward the vacancy by a much larger amount than the calculated 5%. (b) Perhaps there is a larger motion of the three oxygens around Si_{II} than assumed. (c) Perhaps the wave-function amplitudes on Si_{II} are somewhat larger than calculated. We are inclined to disbelieve (a), since this seriously worsens agreement with the magnitudes. (b) may well occur, but (c) seems the simplest and most likely explanation.

In connection with these results, it is important to note that both theoretically and experimentally the major axis of the weak ²⁹Si hyperfine interaction discussed here lies within the plane defined by $Si_0-O_{vacancy}-Si_{II}$ to within a few percent. This observation¹² provides strong qualitative evidence both as to the origin of the interaction (Si_{II}) and the nature of the relaxation (within the above plane).

Table III indicates results of a somewhat exploratory investigation of the origin of the second weak ²⁹Si interaction. Both Si_{VI} and Si_{VIII} were considered as candidates for this interaction. The former is shown in Fig. 1 and its coordinates are given in Ref. 15; Si_{VIII} is not shown, and its coordinates are (-2.7421, 3.7780, 6.8095) bohr, in the system of Ref. 15. Since neither Si_{VI} nor Si_{VIII} was included in the LCLO calculation, the Si_0 wave function was simply orthogonalized to core and valence orbitals on the above atoms. These orthogonalized functions were then used to compute the hyperfine structure (hfs) parameters.

It can be seen that there is moderate agreement with the magnitudes for Si_{VI} , but poor agreement with angle; for Si_{VIII} it is the other way around.

TABLE III. Experimental and calculated hyperfine parameters for the E'_1 center (second weak ²⁹Si interaction).

	Experimental ^b	(c)	(d)
Isotropic hyperfine constant A (in 10 ⁻⁴ cm ⁻¹)	7.46	2.67	0.21
Anisotropic hyperfine constant B_{\parallel} (in 10 ⁻⁴ cm ⁻¹)	1.15	0.42	0.14
Direction of ^a major axis of hyperfine tensor	Experimental Theoretical	42.6° 4.7°	28.3° 19.1°

^aComputed from the hyperfine parameters of Ref. 3. ^bWith respect to ²⁹Si-Si₀ axis.

^cSi_{VI}; wave functions from Ref. 24; Si₀ and Si_{II} displaced from normal as in text; O_{VI} moved by 0.44 Å; Si_{VI} moved 0.3 Å toward O_{VI} .

 Si_{VI} moved 0.3 Å toward O_{VI} . ^dSi_{VIII}; wave functions from Ref. 24; only Si_0 and Si_{II} displaced from normal, as in text.



FIG. 3. (a) C_{2v} model of the E'_1 center. (b) Illustration of A_1 and B_2 modes. (c) Illustration of A_1 and B_2 electronic wave functions.

This is not surprising from the geometry. Si_{VIII} is located away from the hybrid orbital on Si_0 , but the Si_0 - Si_{VIII} direction is in fact close to the experimental hfs major axis. Si_{VI} is on the correct side of the hybrid orbital but its direction to Si_0 is not very close to the experimental hfs major axis.

Since it is difficult to see what modification will provide adequate wave-function density on SivIII, we are inclined to accept Si_{VI} as a better candidate. Two ways of obtaining better agreement with angles would be (a) a large relaxation of Si_{VI} ; (b) asymmetric valence-electron distribution on Sivi. The former seems rather unlikely, since a large (~1 Å) relaxation would be required. (b) seems more likely, and arises from the observation that one of the four oxygens (O_{vI}) neighboring Si_{VI} is inequivalent to the other three, since it is adjacent to the relaxed Si_{II} and may itself be relaxed. Consequently, one expects a wave-function density on Si_{VI} which reflects the actual symmetry next to the defect. This could, for example, lead to a larger electron density towards O_{VI} , since that direction of the crystal is electron deficient. This in turn could have a large effect on the major axis, which would apparently be in the direction of better agreement with experiment.

Finally, it should be noted that our expectation that wave-function components centered on both Si_0 and the other Si_{II} , vI, or vIII would be important was

borne out. For example, for the hyperfine terms due to Si_{II} , wave-function contributions from Si_0 and Si_{II} were of about equal importance. By arbitrarily setting one or the other set equal to zero one could vary the predicted major axis from about 0° to about 28°, as compared with values computed from calculated wave functions ~12° (Table II). Large variations in magnitude were also observed, and in some cases there were interference effects between components. These observations suggest that in general hyperfine data must be used with some care in predicting wave-function densities.

IV. ASYMMETRIC RELAXATION AND PSEUDO-JAHN-TELLER EFFECT

A relaxation which lowers the symmetry of a nonlinear molecule or defect is expected to occur if the electronic states in the symmetric configuration are degenerate, according to the Jahn-Teller theorem.²⁶ Such a relaxation may occur if the electronic states are nondegenerate; this is called a pseudo-Jahn-Teller effect. Recently Ham¹⁶ has analyzed the excited s and p states of the F center in alkali halides, and their coupling through an odd-parity vibrational mode, and has concluded that asymmetric relaxation does not occur in that case. Since we have predicted asymmetric relaxation for the E'_1 center in SiO₂, it is of interest to carry out a similar analysis here.

To make this analysis tractable we adopt an extremely simple model of the E'_1 center, namely, a Si-O_{vacancy}-Si molecule in C_{2v} symmetry as shown in Fig. 3(a). The silicons are constrained to move along the respective Si-O_{vacancy} directions, and the nonbonding orbitals are similarly oriented on the two silicons. Under these circumstances there will be two LCLO's and two vibrational modes, in each case one even and one odd. The even (A_1) and odd (B_2) modes are shown in Fig. 3(b) and the LCLO's in Fig. 3(c).

In terms of our analysis, the relaxation of minimum energy computed in Sec. II corresponds to a minimum with respect to both normal modes. By simple algebra, motion of one silicon toward the vacancy by 5.48% of a nearest-neighbor distance and the other away from the vacancy by 27.4% is the same as an A_1 motion of 10.96% away from the vacancy and a B_2 motion of 16.44%. In the following, only the B_2 coordinate is varied; A_1 is taken as fixed at the above value.

We adopt a notation similar to Ham's. The A_1 electronic state is denoted by s and B_2 by p. The B_2 mode is Q. Note that there is no degeneracy here, whereas in the F center case both the vibrational modes and the p states were threefold degenerate.

The Hamiltonian is taken to be

Parameter	Value	
E_{sb} (eV)	7.61	
$\frac{1}{2}\mu\omega^2$ (eV/Å ²)	17.53	
G (eV/Å)	13.51	
E_{G} (eV)	2.60	

$$H = \frac{1}{2} E_{sp} (|s\rangle\langle s| - |p\rangle\langle p|) + (2\mu)^{-1} [P^2 + (\mu\omega)^2 Q^2] + GQ(|p\rangle\langle s| + |s\rangle\langle p|), \qquad (10)$$

where E_{sp} is the electronic energy difference at Q =0, ω is the angular frequency of the mode, μ is its effective mass, and G is an electron-phonon coupling constant. Following Ham, we analyze the static situation by setting the vibrational momentum P equal to zero and treating Q as a parameter. We find two states whose energies are

$$E = \frac{1}{2}\mu\omega^2 Q^2 \pm \frac{1}{2}(E_{sp}^2 + 4G^2Q^2)^{1/2} .$$
 (11)

The first term of Eq. (11) is just the harmonic oscillator energy, which tends to stabilize the system at Q=0. The second term involves the s-padmixture. For the negative sign this term tends to introduce a minimum away from Q = 0. Note that if E_{sp} were zero this term would be linear in Q and there would always be a minimum away from Q=0; this would be the Jahn-Teller effect.

Ham has shown that the criterion for a minimum away from Q = 0 is

$$E_G > \frac{1}{4} \left| E_{sp} \right| , \qquad (12)$$

where E_G is defined by

$$E_G = G^2 / 2\mu\omega^2 . \tag{13}$$

In this case, the minimum occurs at Q_0 , defined by

$$Q_0^2 = (G/\mu\omega^2)^2 - (E_{sp}/2G)^2 .$$
 (14)

There are thus three parameters which determine the energy in this simplified approach. We have computed the energy using the LCLO-MO method for silicon positions corresponding to several values of Q and have determined values of the parameters with which to fit Eq. (11) to our computed results.

The parameters were determined under the following conditions.

(i) The value of E_{sp} was taken from the computer calculation as the energy difference at Q = 0 between the singly occupied E'_1 state and the first unoccupied state. These states correspond approximately to the A_1 and B_2 states of the model.

(ii) A constant energy was added to Eq. (11) and chosen so that energies at Q = 0 would agree. The value used was 3.80275 eV.

(iii) The value of Q for which the energy is a

minimum, and the value of that energy, were made to agree in the two calculations.

The parameters thus obtained are given in Table IV, and the results are plotted in Fig. 4. Comparison of the theoretical curve (Ham's model) with the computed (LCAO-MO) points indicates fair agreement, with several discrepancies. According to the computations there is, in addition to the energy minima away from Q = 0, a shallow minimum at Q = 0. The simple theory does not predict the coexistence of both types of minima. The computed results also indicate a fair degree of anharmonicity.

It is worth investigating whether the values of the parameters given in Table IV are reasonable. As mentioned earlier, the experimental E'_1 transition energy is at ~ 6.2 eV. This is not directly comparable to E_{sp} , since the latter is computed at an equilibrium position, but the two numbers should probably be (and are) in order-of-magnitude agreement.

The quantity $\frac{1}{2}\mu\omega^2$ is half the force constant for the B_2 mode, so our fit suggests a force constant of 35.06 eV/Å². In this mode the two silicons are weakly coupled and are vibrating in phase, so the "force" is mainly due to the interaction of each silicon with its three neighboring oxygens. For comparison, force constants for diatomics are easily determined²⁷; representative values (in $eV/Å^2$) range from 7.4 for NaCl to 35.3 for AlO, 35.8 for H_2 , 57.7 for SiO, to 118.7 for CO. We can conclude from this that our value of 35.06 seems reasonable.



FIG. 4. Solid line is a plot of the lower solution of Eq. (11) with an added constant (3.80275 eV) so that E = 0 at Q=0, Q is in units of percent of Si-O distance (1.6 Å). Values of the parameters are given in Table IV. Circles are generated from the LCLO-MO solutions.



FIG. 5. Schematic double potential well, as discussed in text.

A very rough estimate of G may be made as follows. The s - p matrix element of the coupling term is just GQ. If one assumed that the admixture was due to a static E field, the corresponding term would be of the form

$$\langle s | \mathcal{H}_{\text{coupling}} | p \rangle \sim eE \langle s | y | p \rangle$$
, (15)

where $\langle s | y | p \rangle$ is an electric-dipole matrix element. When the orbitals are LCLO's one expects the magnitude of $\langle s | y | p \rangle$ to be somewhat less than the Si-Si interatomic distance; ~1-2 Å might be reasonable in our case. One can easily calculate from electrostatics that the *E* field at the oxygen vacancy associated with the *Q* mode, assuming + *e* charge on each silicon, is ~10*Q* V/Å, when *Q* is in Å. Thus we would estimate $G \sim 10-20 \text{ eV}/Å$. Within the accuracy of this rough estimate we find agreement with the calculated value.

The above values may be compared with those obtained in a similar analysis²⁸ of the substitutional off-center Li⁺ ion in KC1. In our notation, these results were $E_{sp} = 4.0 \text{ eV}$; G = 1.25 eV/Å; $\mu\omega^2 = 0.65 \text{ eV}/\text{Å}^2$. In this case the force constant is extremely small, which is consistent with the weak interaction of the small Li⁺ with its neighbors. The coupling constant is an order of magnitude smaller than in our case.

On the basis of the above considerations, we feel that the results of our calculation are reasonable. This does not mean, however, that we feel the numerical results are particularly accurate. Aside from the many approximations made in our LCLO-MO treatment, ¹⁵ one omission is the energy associated with the electronic polarization induced in the atoms outside the cluster by the asymmetric displacement. This has been shown to be important in stabilizing off-center ions in alkali halides, ²⁹ and it would enter the Ham treatment as an in-

crease in the coupling constant *G* (in effect, the *E* field inducing the s - p admixture would be larger). With this in mind, it is interesting to investigate the effect of a small increase in *G* on the results of the analysis performed above. If *G* were 15.0 eV/Å rather than 13.51, for example, the minimum in energy would be~0.53 eV lower than the Q = 0 value, rather than~0.19 eV, and it would occur at $Q \sim 22\%$ rather than~16.4%.

As mentioned earlier, our computer calculations predict that the other well (Si₀ planar, electron on Si_{II}) is actually at an energy lower by ~0.08 eV than the one which we have analyzed and which is experimentally observed. This seems to indicate other errors of the order of tenths of an eV in our calculations.

There remains the question of why experimentally only one well is populated at room temperatures. Presumably, when the defect is created by incident radiation there is enough local thermal agitation that the system spends time in regions of both plus and minus Q, so that the initial probability of being in one or the other is about equal. We suggest a scheme which is consistent with the observed population of only one well, based on double wells, as shown in Fig. 5. We assume that the two wells differ in depth by ~ 0.1 eV and that the lower is ~ 0.5 eV below the value at Q=0. Several vibrational levels are schematically shown. We have sketched the wells so that their minima are ~ 0.3 Å apart.

If the levels in the two wells are in thermal equilibrium with one another, then the population of the ground state of the upper well (*B* in Fig. 5) relative to the ground state of the lower well *A* will be given by a Boltzmann factor which at room temperature for a separation of ~0.1 eV is ~2%. This number is close to the limit of detectability of ESR

spectroscopy for this center.

For the wells to be in thermal equilibrium, however, the probability of tunneling from one to the other must be sufficiently large that tunneling will occur between the time that the system was prepared (e.g., in level *B*) and the ESR experiment was performed. An estimate of this probability may be obtained by multiplying the vibrational frequency ω (the number of times per second that the system attempts to tunnel) by the square of a vibrational wave-function overlap between the two wells.³⁰

The vibrational wave-function overlap depends on the initial and final levels, but it is of order $e^{-a^2/4}$, where

$$a = \Delta Q (\mu \omega^2 / \hbar \omega)^{1/2}$$
 (16)

where ΔQ is the separation in Q of the minima. chosen as ~ 0.3 Å in our case. For this mode it seems reasonable to estimate μ to be twice the mass of Si. For the present value of $\mu\omega^2$ this then yields $\omega \sim 7.6 \times 10^{13}$ sec⁻¹. Then $a \sim 8$, whence the square of the overlap is approximately 10⁻¹⁴. Multiplying this by $\omega \sim 7.6 \times 10^{13}$ sec⁻¹, we obtain a tunneling probability of the order of 1 sec^{-1} , which would appear to be sufficiently large on the time scale of the experiment to ensure thermal equilibrium. It should be emphasized that all of these numbers are very rough, used only to estimate the plausibility of this model. Alternative theoretical estimates of the tunneling probability between wells (e.g., based on a more detailed vibronic theory) may be made, but all require a to be ~8-10 for a

tunneling probability of $\sim 1 \text{ sec}^{-1}$.

If this model is correct, it would appear that by going to either higher or lower temperatures one could expect to observe the effect of the second minimum in the paramagnetic resonance response. At high temperatures the Boltzmann factor would increase the probability of the system's being in *B*; at low temperatures one would expect the tunneling probability to decrease sharply—hence a center prepared in state *B* might remain there long enough to be observed experimentally.

V. E'_1 (Ge) CENTER IN SiO₂

The E'_1 (Ge) center is another version of the E'_1 center in which an electron is trapped by a germanium atom substituted for a silicon atom neighboring an oxygen vacancy in SiO₂. The EPR response of this center, reported by Feigl and Anderson,⁵ is very similar to that of the simple E'_1 center in pure SiO_2 . It has been suggested that the unpaired electron occupies a nonbonding sp^3 orbital strongly localized on a Ge impurity.⁵ Since the basic electronic structure of the E'_1 (Ge) center is quite similar to the simple E'_1 center, it seems reasonable to use the same asymmetrical relaxed oxygen vacancy model presented in Sec. IV to explain the observed hyperfine data. To do this, a similar calculation on an eight-atom cluster $GeSiO_6$, in which the Si_0 atom is substituted by a Ge atom [see Fig. 1(b), was performed. The basis functions for the Ge⁺⁺ ion in the $Si^{++}(O^{-})_2$ lattice were obtained by solving the following localized orbital equations (in integral form):

$$\begin{aligned} \epsilon_{4s} &= K_{4s} + 2F^{0}(4s, 1s) + 2F^{0}(4s, 2s) + 2F^{0}(4s, 3s) + 2F^{0}(4s, 4s) + 6F^{0}(4s, 2p) + 6F^{0}(4s, 3p) + 10F^{0}(4s, 3d) \\ &- G^{0}(4s, 1s) - G^{0}(4s, 2s) - G^{0}(4s, 3s) - G^{0}(4s, 4s) - G^{1}(4s, 2p) - G^{1}(4s, 3p) - G^{2}(4s, 3d) + V_{4s} , \\ \epsilon_{4p} &= K_{4p} + 2F^{0}(4p, 1s) + 2F^{0}(4p, 2s) + 2F^{0}(4p, 3s) + F^{0}(4p, 4s) + 6F^{0}(4p, 2p) + 6F^{0}(4p, 3p) + F^{0}(4p, 4p) \\ &+ 10F^{0}(4p, 3d) - \frac{1}{3}G^{1}(4p, 1s) - \frac{1}{3}G^{1}(4p, 2s) - \frac{1}{3}G^{1}(4p, 3s) - \frac{1}{6}G^{1}(4p, 4s) - G^{0}(4p, 2p) - \frac{2}{3}G^{2}(4p, 2p) \\ &- G^{0}(4p, 3p) - \frac{2}{5}G^{2}(4p, 3p) - G^{0}(4p, 4p) - \frac{2}{3}G^{1}(4p, 3d) - \frac{3}{7}G^{3}(4p, 3d) + V_{4p} . \end{aligned}$$

In Table V, we specify the basis parameters A_{Ij} and Z_{Ij} used for Ge⁺⁺ in SiO₂ and also give their oneelectron eigenvalues ϵ_{nI} and eigenfunctions C_{jnI} and the expectation values of the atomic environment potential U_a and the Fock operator F. All these terms have been defined in the previous papers.^{14,15}

In calculating the matrix elements of the Fock operator, corrections arising from the absence of an oxygen ion were taken into account. Little effort was expended to locate the most probable relaxed atomic arrangement which has the minimum of total system energy. In this calculation, the same relaxation as obtained from the E'_1 -center calculation was assumed.

The MO energy levels for the relaxed GeSiO_6 cluster are shown in Fig. 2, as compared with those of the relaxed Si_2O_6 cluster. The calculated wave function for the E_1' (Ge) unpaired electron is

$$\psi(E'_{1}, (Ge) = 0.5415\varphi_{Ge\,4s} + 0.7856\varphi_{Ge\,4p_{x}} + 0.1194\varphi_{Ge\,4p_{y}} + 0.3381\varphi_{Ge\,4p_{z}} + 0.0136\varphi_{Si_{II}\,3s} + 0.1190\varphi_{Si_{II}\,3p_{x}} - 0.0180\varphi_{Si_{II}\,3p_{y}} + 0.0262\varphi_{Si_{II}\,3p_{z}} + \text{other terms for oxygen atoms} .$$
(18)

2336

.

TABLE V. Atomic parameters and energy parameters (in Ry) for Ge^{**} in SiO_2 .^a

j	A_{0j}	Z_{0j}	C_{j40}	A_{1j}	Z_{1j}	C _{j41}	
1	0	33,9345	0.02817	0	21.1223	0.00917	
2	1	30,0221	0.01923	0	13.6615	0.07134	
3	1	15,5531	-0.07585	1	12.9671	0.02392	
4	2	14.7273	-0.07729	1	8,3249	- 0.07573	
5	2	7,4622	-0.17180	1	5.2291	-0.21223	
6	2	5,7676	0.77794	2	4.7359	0.03100	
7	3	5,9822	-0.31172	2	2.2704	0.58835	
8	3	3.0892	-0,23799	2	1.2458	0.62720	
9	3	2.0145	-0.76187	2	0.8512	-0.15684	
10	3	1.3508	-0.07008				
$\epsilon_{40} = -2.413707$				$\epsilon_{4b} = -1.829256$			
	$V_{4s}^{4s} = 0.421155$ $\epsilon_{4s,4s} = -1.992552$				$V_{40} = 0.444380$		
					$\epsilon_{4p,4p} = -1.384876$		

^aThe values for A_{1j} and Z_{1j} were chosen from Ref. 31.

Using this wave function for the E'_1 (Ge) center, it can be shown that

(i) The electron density distribution in $\psi(E'_1, \text{Ge})$ is $\text{Ge}(4s^{0.17}4p^{0.54})\text{Si}_{II}(3s^{0.001}3p^{0.006})$; this implies that the unpaired electron spends 71% of its time on Ge compared with 0.8% on Si_{II}.

(ii) The unpaired electron which is strongly localized on the Ge impurity occupies a nonbonding $\sim sp^{3\cdot 1}$ hybrid orbital of 17% atomic 4s character and 54% atomic 4p character.

(iii) The $sp^{3\cdot 1}$ orbital is oriented almost along the Ge - O_{II} short-bond direction to within 0.01%.

These results are generally consistent with the observed hyperfine interaction and anisotropic g-tensor data.⁵ We have not analyzed the weak hyperfine interactions in detail.

From the MO energy-level diagram (Fig. 2) for the E'_1 (Ge) center, an optical absorption is predicted to occur at 4.0 eV. Although there are no ultraviolet data available for comparison, it serves as an indicator for future experimental optical studies for this center.

VI. CONCLUSIONS

It has been shown that the previously developed LCLO-MO cluster method has given satisfactory quantum-mechanical descriptions of the electronic structures of E'_1 centers in SiO₂. We conclude that present experimental and theoretical evidence indicate the following.

(a) The E'_1 center is an O⁻ vacancy and is therefore positively charged. It can be thought of as a hole trapped at a neutral oxygen vacancy. Its properties are best understood, however, in terms of the remaining nonbonding electron. In the terminology adopted for simpler oxides, the E'_1 center is an F^+ center.

(b) A highly asymmetric relaxation of the two silicons adjacent to the O⁻ vacancy occurs.¹²

(c) The defect electron is strongly localized (~82%) in a nonbonding sp^3 hybrid orbital centered on a silicon and oriented almost along a Si-O shortbond direction toward the oxygen vacancy.

(d) The experimental hyperfine data are reasonably consistent with the predictions of our model. This is a critical test of the model.

(e) The asymmetric relaxations may be analyzed by means of the theory of the pseudo-Jahn-Teller effect. This analysis suggests that both low- and high-temperature EPR experiments might be useful.

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