MODEL FOR THE E_1' CENTER IN SiO_2

A. R. Ruffa
Naval Research Laboratory, Washington, D. C. 20390

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A theoretical model is presented for both the permanent and transient E_1' centers in SiO_2 together with a mechanism for their optical excitation. The model presented involves the Heitler-London description of Si-O bonding. Experimental tests for verification of the model are discussed in some detail.

The E_1' center is a radiation-induced paramagnetic defect in both crystalline and glassy SiO_2 which was first reported by Nelson and Weeks.[1] The center was observed to be permanent with an optical-absorption peak at about 5.7 eV. Subsequently, Griscom and Sigel[2] observed what appears to be the same center produced transiently by pulsed high-energy electrons. While there is some disagreement about the detailed interpretation of the spin-resonance data, there seems to be general agreement that the observed paramagnetic resonance is produced by an unpaired silicon sp^3 hybrid orbital.[3] This conclusion is based upon the magnitude of the hyperfine interaction of the electron with the Si^{29} nucleus.

With this information in hand, there are certain conclusions which can be drawn on purely theoretical grounds:

(1) If the transient center does indeed resemble the permanent center in that it involves a dangling Si sp^3 orbital, then the creation of the transient center would appear to be a purely electronic process. This is because it appears unlikely that a transient process could involve the breaking of bonds and the production of a large void in the material. (The simple removal of an O atom is not sufficient to produce the center for reasons which will be discussed below.)

(2) The center must involve a Si atom bonded to three O atoms with the remaining hybrid orbital forming the E_1' center. Fewer bonds would produce an energetically unstable situation due to the large energy of hybridization of the Si atom. This energy can be calculated approximately for the Si atom in the solid material by determining the weighted energy differences between the $3s^23p^2$ and the $3s3p^3$ configurations as obtained from atomic spectra tables. The result is 5.4 eV. Comparing this with the 7.9 eV Si-O bond energy determined from thermochemical data,[4] we see that hybridization to produce three bonds creates a stable arrangement. However, a two-bond arrangement is highly unstable, and the Si atom would strongly favor the nonhybrid configuration, with the two p orbitals forming the two bonds.

(3) The center cannot be produced by the simple removal of an O atom, since the two Si hybrid orbitals projecting into the vacancy have a large overlap (the calculated value of the overlap integral is 0.42). Such a situation would result in a strongly bound singlet state. Removal of one of the electrons in these orbitals cannot be a mechanism for the production of the permanent center, since the remaining electron would tend to resonate between the two Si atoms, and the hyperfine interaction would be smaller than that observed. This could, however, be a mechanism for the formation of the transient center, and an experimental test would be the examination of the hyperfine interaction of its ground state.

With this as a background, it is clear that the first steps in forming a model for the E_1' center must be consistent with the above considerations, provide a mechanism which is in reasonable agreement with the optical absorption at 5.7 eV, and be relatively insensitive in this result to local distortions of the environment such as occur in the glassy material. Such a model can then be used to make predictions of experimental results which can be used as tests of its validity. The model for the permanent center which will be considered here consists of a single hybrid Si orbital projecting into a void which does not contain any electrons in overlapping orbitals. Detailed mechanisms for producing this situation will not be analyzed, but the center will be viewed generally as a sort of surface effect. Some possibilities which seem reasonable are that the center would exist (a) at the surface of the bulk material or microparticles within the material, (b) at a large defect such as a dislocation, or (c) in the vicinity of another Si atom bonded to only two O atoms and not having any remaining unpaired orbitals. The last situation could take place in an area of local lattice distortion where a Si atom in the s^2p^2 configuration and bonded to only two O atoms would represent a more stable arrangement than that involving a Si atom in the hybrid configuration which is imperfectly bonded to three O atoms.

The mechanism for the excitation of this defect will be discussed within the framework of the localized valence bond picture proposed earlier[4] for analyzing the ultraviolet spectrum of quartz. Bonding within this approximation is accomplished by means of two-electron Heitler-London subwave functions of the form

$$\psi_b(1,2)=2^{-1/2}[\psi_{\mathrm{Si}}(1)\psi_{\mathrm{O}}(2)+\psi_{\mathrm{O}}(1)\psi_{\mathrm{Si}}(2)]\times[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \tag{1}$$

embedded in a generalized antisymmetric product wave function for the whole material. An effective Hamiltonian acts upon the two electrons, having the form

$$H'(1,2)=H(1)+H(2)+1/R_{12}+1/R_{\mathrm{SiO}}, \tag{2}$$

where R_{12} is the interelectronic distance, R_{SiO} is the internuclear distance, and $H(1)$ and $H(2)$ operate on electrons 1 and 2, respectively, and have the form

$$H=\frac{-\nabla^2}{2}-\frac{K_1(R)}{R_{\mathrm{Si}}}-\frac{K_2(R)}{R_{\mathrm{O}}}. \tag{3}$$

The quantities $K_1(R)$ and $K_2(R)$ are the effective charges which the electron sees on each nucleus, and thus vary with the electronic coordinate. The energy which one obtains from the wave function (1) and the Hamiltonian (2) is

$$E=E_{\mathrm{Si}}+E_{\mathrm{O}}+E_b=E_{\mathrm{Si}}+E_{\mathrm{O}}+\frac{J+K}{1+S^2}, \tag{4}$$

where E_{Si} and E_{O} are the one-electron energies of the Si and O orbitals, S is their overlap integral, E_b is the Heitler-London bond energy while J and K, which yield the Coulomb and exchange energies, are given by

$$K=\frac{S^2}{R_{\mathrm{SiO}}}+\left(\psi_{\mathrm{Si}}(1)\psi_{\mathrm{O}}(1),\ \frac{1}{R_{12}}\psi_{\mathrm{Si}}(2)\psi_{\mathrm{O}}(2)\right)-S\left[\bar{K}_2\left(\psi_{\mathrm{Si}_1},\frac{1}{R_{\mathrm{O}}}\psi_{\mathrm{O}}\right)+\bar{K}_1\left(\psi_{\mathrm{Si}},\frac{1}{R_{\mathrm{Si}}}\psi_{\mathrm{O}}\right)\right] \tag{5}$$

and

$$J=-\bar{K}_{\mathrm{C}}\left[\left(\psi^2{}_{\mathrm{Si}},\frac{1}{R_{\mathrm{O}}}\right)+\left(\psi_{\mathrm{O}}{}^2,\frac{1}{R_{\mathrm{Si}}}\right)\right]+\frac{1}{R_{\mathrm{SiO}}}+\left(|\psi_{\mathrm{Si}}(1)|^2,\frac{1}{R_{12}}|\psi_{\mathrm{O}}(2)|^2\right), \tag{6}$$

where average values of the effective charges $\bar{K}_2$ and $\bar{K}_1$ are brought outside the integrals in (5) and an average value $\bar{K}_{\mathrm{C}}$ which is close to unity is used in (6).

The detailed model for excitation to be considered quantitatively is as follows. One Si-O bond is broken and the Si atom is demoted from the excited sp^3 state to the s^2p^2 configuration. The two remaining bonds are formed from Si $3p$ orbitals which are inclined at about a 10° angle from the bond axes. This is because the p orbitals are separated by 90° while the bond axes are separated by nearly 110°. The greatest stability is achieved when the two orbitals are separated from their bond axes by equal amounts. In the original Si-O bond, the O $2p$ bonding orbital is inclined at an angle of about 27° from the bond axis since the Si-O-Si bond angle is 144°. After one bond is broken, the remaining bond can be stabilized by alignment of the $2p$ orbital along the bond axis.

The calculations of the necessary bond energies have been made by means of Eqs. (4), (5), and (6). The one-electron two-center integrals appearing in the exchange energy were evaluated by means of elliptical coordinates using the Slater[5] silicon $3s$ and $3p$ and oxygen $2p$ orbitals. The two-electron two-center integral was evaluated by means of Mulliken's[6] approximation. The integrals appearing in the Coulomb energy were evaluated by determining the classical electrostatic interaction energy between the charge densities of the bonding orbitals by making the appropriate multipole expansions. This approximation was examined in some detail by Mulligan[7] who found it fairly accurate even for nearest neighbors.

The effective screening constants $\bar{K}_1$ and $\bar{K}_2$ were evaluated by requiring the Hamiltonian to be Hermitean, which leads to the equality

$$(\psi_{\mathrm{Si}},H\psi_{\mathrm{O}})=(\psi_{\mathrm{O}},H\psi_{\mathrm{Si}}), \tag{7}$$

where H is given by (3). This yields the relation

$$S(E_{\mathrm{O}}-E_{\mathrm{Si}})=\bar{K}_2\left(\psi_{\mathrm{O}},\frac{1}{R_{\mathrm{O}}}\psi_{\mathrm{Si}}\right)-\bar{K}_1\left(\psi_{\mathrm{O}},\frac{1}{R_{\mathrm{Si}}}\psi_{\mathrm{Si}}\right). \tag{8}$$

The one-electron energies used in (8) are those given by Herman and Skillman[8] with the value for the one-electron Hamiltonian, i.e., $E_{sp^3}=E_{3s}/4+3E_{3p}/4$.

By assuming that $\bar{K}_1$ and $\bar{K}_2$ are the same whether bonding involves a Si $3p$ or hybrid orbital, two equations of the form (8) result for $\bar{K}_1$ and $\bar{K}_2$ which yield the values $\bar{K}_1=3.12$ and $\bar{K}_2=2.81$. This enables one to get a unique value for the exchange energy. The constant $\bar{K}_{\mathrm{C}}$ is then determined by setting the total Heitler-London

Table I. Energy of excitation of proposed E_1'-center model.

Break one bond	7.9 eV
Weaken two Si-O bonds	3.4 eV
Demote Si atom to s^2p^2 configuration	−5.4 eV
Stabilize remaining Si-O bond	−0.8 eV
Calculated total energy of excitation	5.1 eV

bond energy equal to the value 7.9 eV obtained from thermochemical data. The value obtained is $\overline{K}_C = 1.177$.

The result of the complete calculation is summarized in Table I. The calculated energy of excitation is 5.1 eV, in reasonably good agreement with the observed value of 5.7 eV. One may also note that the relatively small stabilization energy of 0.8 eV when the O $2p$ orbital is aligned along the bond axis implies very little hybridization of the O atom in spite of the large 144° Si-O-Si bond angle. An attractive feature of the result is that the calculated bond energies are not extremely sensitive to distortion of bond angles. This helps explain why the optical spectra of glassy and crystalline SiO_2 are so similar.

A decisive test of this model could be made by examining the spin resonance of the excited state. It should, according to this model, exhibit a strong spin resonance but no hyperfine interaction with the Si^{29} nucleus. Rather, a strong hyperfine interaction with an O^{17} nucleus should be observed in an enriched sample, since the only unpaired electron is in an O $2p$ orbital. If the transient center is indeed created by removing a Si hybrid orbital from an O vacancy, the favored process appears to involve the breaking of one of the Si-O bonds and the demotion of the Si atom back to its ground state, since completer removal of the electron while leaving behing three bonding electrons would require on the order of 10 eV. This is because the lowest such excited state of Si, which has the sp^2 configuration, lies 7.6 eV above the sp^3 hybrid state. In addition, because the sp^2 orbitals are not directed along the bond axis, there is an additional energy loss of the order of 2 eV for the three bonds. For the excitation process involving the breaking of a bond and demotion of a Si atom, there would be no overlap with the remaining dangling Si hybrid orbital and the situation might be quite similar to that which could be created permanently by lattice distortion. The permanent and transient centers would then be expected to behave quite similarly except for the difference in the hyperfine interaction in the ground state as discussed above.

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