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Electronic band structure of stishovite (tetragonal SiO_2)

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We have calculated the valence-band structure of stishovite, a tetragonal form of SiO_2, using a simple tight-binding method. As in similar fits to computed valence bands in α-quartz and β-cristobalite, only oxygen orbitals are used in the basis set. Values of the tight-binding parameters are based on the earlier calculations. A direct forbidden optical edge is predicted, as found in other tetragonal oxides of group-IV elements. There is no gap between bonding and nonbonding valence bands, in contrast to forms of SiO_2 which exhibit twofold oxygen coordination. Implications regarding the electronic structure of a-SiO_2 are discussed.

I. INTRODUCTION

We use a simple tight-binding method to investigate the valence-band structure of a tetragonal form of silicon dioxide called stishovite. The procedure is originally due to Slater and Koster.[1] We assume an ionic model for stishovite so that the valence band originates from $2s$ and $2p$ orbitals of oxygen. The method requires a small basis set and is thus a simple one for stishovite which has a low symmetry and a large unit cell. It can be applied at an arbitrary point in the Brillouin zone, and the solutions have all the correct symmetry properties. This method has been used for other forms of crystalline silicon dioxide with remarkable success.[2,3]

We have shown elsewhere[4] that this version of tight-binding theory using a basis set of atomic orbitals can be justified in terms of a modified chemical pseudopotential (CP). Our version of CP seems to be better suited for this purpose than the usual CP of Anderson and Bullett.[5,6]

Among the polymorphs of SiO_2, stishovite is the least known form. It is found in small quantities in meteors[7] and can be artificially made in the laboratory.[8] It is one of the products of shock-loaded quartz.[9] Study of this material is important, like any other polymorph of SiO_2, for a better understanding of amorphous SiO_2. No experimental or theoretical work has yet been reported[10] which bears on the electronic properties of stishovite.

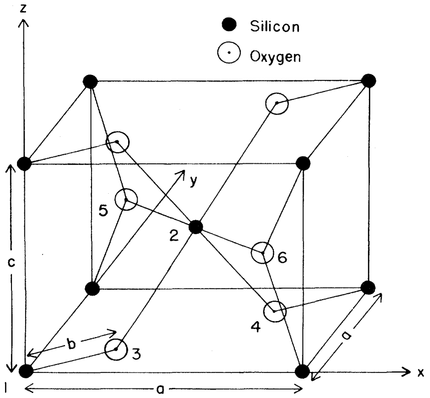

FIG. 1. Unit cell of stishovite. Values for a, b, and c are given in the text.

In our simple approach the values of the required tight-binding parameters will be determined by scaling the parameters from other polymorphs of SiO_2. We will also consider the results for other materials of interest. A good number of experimental and theoretical results are available for several tetragonal crystals of dioxides of group-IV elements having the same structure as that of stishovite,[11–17] i.e., SnO_2, GeO_2, PbO_2, and TiO_2. For all these oxides the bottom of the conduction band and the top of the valence band have been found to be of Γ_1^+ and Γ_3^+ symmetry, respectively, with direct forbidden optical edges.[16,17] Tetragonal SiO_2 is a good candidate to be investigated along the same lines.

II. STRUCTURE

Stishovite has the rutile structure, shown in Fig. 1, which has the space group D_{4h}^{14}. The unit cell is tetragonal with primitive translation vectors

$$\vec{a}_1=(a,0,0)\ ,$$

$$\vec{a}_2=(0,a,0)\ ,$$

$$\vec{a}_3=(0,0,c)\ ,$$

where $a=4.179$ Å and $c=2.665$ Å.[18] Vectors $\vec{a}_1$ and $\vec{a}_2$ are along the x and y axis, respectively, both having length a, and $\vec{a}_3$ is along the z axis and has length c. The unit cell contains six atoms, two silicons (denoted by 1 and 2) and four oxygens (denoted by 3, 4, 5, and 6) at the following positions:

Si (1): $\vec{d}_1=(0,0,0)\ ,$

Si (2): $\vec{d}_2=(a/2,a/2,c/2)\ ,$

O (3): $\vec{d}_3=(b/\sqrt{2},b/\sqrt{2},0)\ ,$

O (4): $\vec{d}_4=(a-b/\sqrt{2},a-b/\sqrt{2},0)\ ,$

O (5): $\vec{d}_5=(a/2-b/\sqrt{2},a/2+b/\sqrt{2},c/2)\ ,$

O (6): $\vec{d}_6=(a/2+b/\sqrt{2},a/2-b/\sqrt{2},c/2)\ ,$

with $b = 1.810$ Å.[18] Each silicon atom is surrounded by six oxygen atoms in the form of a slightly distorted octahedron. Each oxygen atom has three neighboring silicons lying in a plane forming an isosceles triangle. There are two different O-Si distances, b and

$$[2(a/2 - b/\sqrt{2})^2 + (c/2)^2]^{1/2} ,$$

and three different O-O distances, $\sqrt{2}(a - \sqrt{2}b)$, c, and

$$[(a/2 - \sqrt{2}b)^2 + (a/2)^2 + (c/2)^2]^{1/2} .$$

The octahedra become ideal if

$$(c/a) = \sqrt{2}(b/a) = 2 - \sqrt{2} .$$

The reciprocal lattice is also tetragonal, formed by the vectors

$$\vec{A}_1 = (2\pi/a, 0, 0) ,$$

$$\vec{A}_2 = (0, 2\pi/a, 0) ,$$

$$\vec{A}_3 = (0, 0, 2\pi/c) ,$$

and is shown in Fig. 2.

The space group D_{4h}^{14} is nonsymmorphic and has 16 symmetry operations associated with it. Analysis of this group has been done by Dimmock *et al.*,[19] Gay *et al.*,[20] and also by Albert *et al.*[21] The relationship between the works of Ref. 19 and Ref. 20 and further details on the rutile structure are presented by Mattheiss.[22] The notations used by us are those of Ref. 20. Since we will be interested mainly in the Γ point, the symmetrized linear combinations of s and p orbitals[21] at that point are given in Table I.

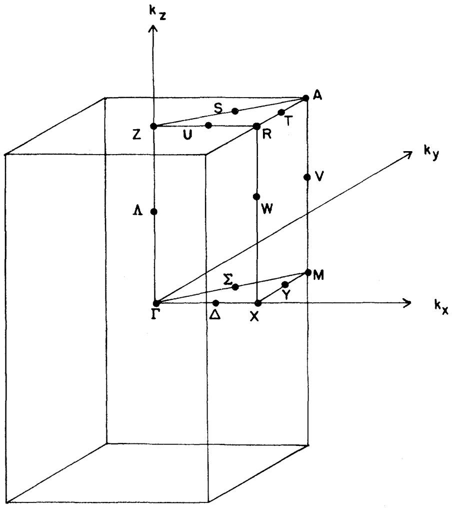

FIG. 2. Brillouin zone of simple tetragonal lattice.

III. THE BASIS SET

The band structure and the energy gap of a material reflect the covalency or ionicity in the tight-binding sense. In an ionic model for stishovite little bonding occurs among the orbitals of the constituent ions and the energy band maintains to a large extent the order in energies of the free-ion orbitals shifted by the Madelung well. So the valence band will be composed of oxygen 2s and 2p orbitals, the ionic effects will open up the gap and the bottom of the conduction band will be mainly silicon 3s-like. The 1s orbital of oxygen and the 1s, 2s, and 2p orbitals of silicon are fairly localized and have large binding energy, so we can neglect them. However, there will be considerable overlap between the diffuse O 2s and 2p and Si 3s and 3p orbitals. But these overlap interactions can be neglected due to strong ionic effects which shift the energies of the orbitals away from one another. So it is a good approximation to treat only O 2s and 2p orbitals which lie far from the energy regions of all other orbitals.

Such a model describing the valence band by O 2s and 2p orbitals has worked remarkably well for α-quartz[2] and β-cristobalite.[3] In the case of stishovite where an sp^3 bond picture is not plausible, an ionic model is even more appropriate. Detailed calculations on energy-band structures

TABLE I. The symmetrized linear combinations of the O 2s and 2p orbitals (Ref. 21) at the Γ point. s,x,y,z denote s,p_x,p_y,p_z functions. Subscripts $1,2,\ldots,6$ denote the atoms on which the orbitals are centered.

Γ_1^+: $s_3+s_4+s_5+s_6$; $x_3-x_4-x_5+x_6+y_3-y_4+y_5-y_6$

Γ_2^+: $x_3-x_4+x_5-x_6-y_3+y_4+y_5-y_6$

Γ_3^+: $x_3-x_4-x_5+x_6-y_3+y_4-y_5+y_6$

Γ_4^+: $s_3+s_4-s_5-s_6$; $x_3-x_4+x_5-x_6+y_3-y_4-y_5+y_6$

Γ_5^+: s_3-s_4, s_5-s_6; $x_3+x_4-y_3-y_4$, $-x_5-x_6-y_5-y_6$;
$x_3+x_4+y_3+y_4$; $-x_5-x_6+y_5+y_6$

Γ_1^-: $z_3+z_4+z_5+z_6$

Γ_4^-: $z_3+z_4-z_5-z_6$

Γ_5^-: z_3-z_4, z_5-z_6

of other dioxides of group-IV elements having the rutile structure support this view. In SnO_2,[17] for example, the top of the valence band is made of O $2p$ lone-pair states and the lowest conduction band is 90% Sn s-like. The valence-band density of states for SnO_2 has very little contribution from Sn orbitals. The lone-pair-type O $2p$ orbitals are perpendicular to the bonding plane of neighboring silicons.

IV. THE TIGHT-BINDING METHOD

Bloch sums are made from each of the orbitals s, p_x, p_y, and p_z situated on four oxygen atoms in the unit cell:

$$|\psi_{\alpha i}^{\vec{k}}\rangle = \frac{1}{(\Omega_{\alpha i}^{\vec{k}})^{1/2}} \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha)} |\varphi_{\alpha i}^{\vec{R}}\rangle . \tag{1}$$

The sum is carried over the lattice vectors $\vec{R}$. $|\varphi_{\alpha i}^{\vec{R}}\rangle$ is an orbital centered on the oxygen site at $(\vec{R}+\vec{d}_\alpha)$, $\vec{d}_\alpha$ denoting the position of an oxygen atom α ($\alpha=3,4,5,6$) in the unit cell. i is the quantum index specifying s, p_x, p_y, or p_z. $1/(\Omega_{\alpha i}^{\vec{k}})^{1/2}$ is the normalization constant, requiring that

$$\langle \psi_{\alpha i}^{\vec{k}} | \psi_{\alpha i}^{\vec{k}} \rangle = 1 , \tag{2}$$

or,

$$\frac{N}{\Omega_{\alpha i}^{\vec{k}}} \sum_{R} e^{i\vec{k}\cdot\vec{R}} \langle \varphi_{\alpha i} | \varphi_{\alpha i}^{\vec{R}} \rangle = 1 , \tag{3}$$

or,

$$\Omega_{\alpha i}^{\vec{k}} = N \left[1 + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \langle \varphi_{\alpha i} | \varphi_{\alpha i}^{\vec{R}} \rangle \right] , \tag{4}$$

where N is the number of unit cells.

Notice that the normalization constants contain overlaps between identical orbitals which are lattice vectors apart. $|\psi_{\alpha i}^{\vec{k}}\rangle$'s are not orthogonal to one another because of the overlaps between the orbitals on different sites:

$$\langle \psi_{\beta j}^{\vec{k}} | \psi_{\alpha i}^{\vec{k}} \rangle = \frac{N}{(\Omega_{\beta j}^{\vec{k}} \Omega_{\alpha i}^{\vec{k}})^{1/2}} \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)} \langle \varphi_{\beta j} | \varphi_{\alpha i}^{\vec{R}} \rangle . \tag{5}$$

These overlaps are not desirable quantities in an empirical tight-binding[23] study such as the one we are performing and can be removed from the secular equation using a chemical pseudopotential (CP) approach.[4-6]

We define the basis orbitals $|\varphi_{\alpha i}^{\vec{R}}\rangle$ as the self-consistent solutions of the CP equation[4]

$$\left[T + V_\alpha^{\vec{R}} + \left[U_\alpha^{\vec{R}} - \sum_{\vec{Q}} \sum_{\beta} \sum_{j} |\varphi_{\beta j}^{\vec{Q}}\rangle \langle \varphi_{\beta j}^{\vec{Q}} | U_\alpha^{\vec{R}} \right] \right] |\varphi_{\alpha i}^{\vec{R}}\rangle = E_{\alpha i} |\varphi_{\alpha i}^{\vec{R}}\rangle , \tag{6}$$

where T is the kinetic energy operator, $V_\alpha^{\vec{R}}$ is the spherically symmetric potential centered on the oxygen at $(\vec{R}+\vec{d}_\alpha)$, and $U_\alpha^{\vec{R}} = \mathscr{H} - T - V_\alpha^{\vec{R}}$, $\mathscr{H}$ being the total crystal Hamiltonian. $E_{\alpha i}$ $(=E_i)$ is the energy eigenvalue of Eq. (6). The above Eq. (6) is somewhat different from the usual CP equation of Anderson and Bullett,[5,6] in that we have projected out more of the "environment" potential to define the localized orbitals than is done in the usual CP scheme. The solutions $|\varphi_{\alpha i}^{\vec{R}}\rangle$ and $E_{\alpha i}$ of the CP equation are approximately the same as the corresponding quantities in the atomic picture. From Eq. (6) we have

$$\mathscr{H} |\varphi_{\alpha i}^{\vec{R}}\rangle = E_{\alpha i} |\varphi_{\alpha i}^{\vec{R}}\rangle + \sum_{\vec{Q}} \sum_{\beta} \sum_{j} \langle \varphi_{\beta j}^{\vec{Q}} | U_\alpha^{\vec{R}} | \varphi_{\alpha i}^{\vec{R}} \rangle |\varphi_{\beta j}^{\vec{Q}}\rangle , \tag{7}$$

and using Eq. (1),

$$\mathscr{H} |\psi_{\alpha i}^{\vec{k}}\rangle = \sum_{\beta} \sum_{j} \left[\frac{\Omega_{\beta j}^{\vec{k}}}{\Omega_{\alpha i}^{\vec{k}}} \right]^{1/2} H_{\beta j,\alpha i}(\vec{k}) |\psi_{\beta j}^{\vec{k}}\rangle , \tag{8}$$

where

$$H_{\beta j,\alpha i}(\vec{k}) = E_{\alpha i} \delta_{\alpha\beta} \delta_{ij} + \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)} \langle \varphi_{\beta j} | U_\alpha^{\vec{R}} | \varphi_{\alpha i}^{\vec{R}} \rangle . \tag{9}$$

An eigenfunction for our problem at an arbitrary value of $\vec{k}$ is a linear combination of the Bloch sums,

$$|\psi_{\vec{k}}\rangle = \sum_{\alpha} \sum_{i} a_{\alpha i} |\psi_{\alpha i}^{\vec{k}}\rangle, \quad \mathscr{H} |\psi_{\vec{k}}\rangle = E_{\vec{k}} |\psi_{\vec{k}}\rangle , \tag{10}$$

where $E_{\vec{k}}$ is the energy eigenvalue. Combining Eqs. (8) and (10) we get

$$\sum_{\beta} \sum_{j} \left\{ \sum_{\alpha} \sum_{i} a_{\alpha i} \left[\left[\frac{\Omega_{\beta j}^{\vec{k}}}{\Omega_{\alpha i}^{\vec{k}}} \right]^{1/2} H_{\beta j,\alpha i}(\vec{k}) - E_{\vec{k}} \delta_{\alpha\beta} \delta_{ij} \right] \right\} |\psi_{\beta j}^{\vec{k}}\rangle = 0 . \tag{11}$$

Since the $|\varphi_{\beta j}^{\vec{R}}\rangle$'s do not form an overcomplete set, the $|\psi_{\beta j}^{\vec{k}}\rangle$'s are linearly independent. The energy eigenvalues are obtained by solving the secular equation

$$\det | H_{\beta j,\alpha i}(\vec{k}) - E_{\vec{k}} \delta_{\alpha\beta} \delta_{ij} | = 0 . \tag{12}$$

The secular equation is completely overlap-reduced and the problem is amenable to suitable parametrization. $H_{\beta j,\alpha i}(\vec{k})$ can be written as

$$H_{\beta j,\alpha i}(\vec{k})=E_{\alpha i}\delta_{\alpha\beta}\delta_{ij}+\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\langle\varphi_{\alpha j}\,|\,U_\alpha^{\vec{R}}\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle\delta_{\alpha\beta}+\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)}\langle\varphi_{\beta j}\,|\,U_\alpha^{\vec{R}}\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle(1-\delta_{\alpha\beta})\,, \tag{13}$$

$$\begin{aligned}H_{\beta j,\alpha i}(\vec{k})={}&E_{\alpha i}\delta_{\alpha\beta}\delta_{ij}+\langle\varphi_{\alpha j}\,|\,U_\alpha\,|\,\varphi_{\alpha i}\rangle\delta_{\alpha\beta}+\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\langle\varphi_{\alpha j}\,|\,U_\alpha^{\vec{R}}\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle\delta_{\alpha\beta}\\&+\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)}\langle\varphi_{\beta j}\,|\,U_\alpha^{\vec{R}}\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle(1-\delta_{\alpha\beta})\,.\end{aligned} \tag{14}$$

Here $U_\alpha^{\vec{R}}$ is the sum of the potentials of all the atoms except that of the oxygen at $(\vec{R}+\vec{d}_\alpha)$. In the second term we make the approximation $U_\alpha=\sum_s V_s$ where $\sum_s V_s$ is the sum of the potentials of the three neighboring silicons. We consider only two-center integrals, and the summation over $\vec{R}$ is carried through terms such that the distance between two centers is always less than c (=2.665 Å). Therefore, the third term vanishes and $U_\alpha^{\vec{R}}=V_\beta$ in the fourth term. Hence,

$$\begin{aligned}H_{\beta j,\alpha i}(\vec{k})={}&E_{\alpha i}\delta_{\alpha\beta}\delta_{ij}+\langle\varphi_{\alpha j}\,|\,\sum V_s\,|\,\varphi_{\alpha i}\rangle\delta_{\alpha\beta}\\&+\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)}\langle\varphi_{\beta j}\,|\,V_\beta\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle(1-\delta_{\alpha\beta}),\quad |\vec{R}+\vec{d}_\alpha-\vec{d}_\beta|<c\,.\end{aligned} \tag{15}$$

There are two types of integrals in the matrix H:

$$\begin{aligned}&a\text{ type: }\ \langle\varphi_{\alpha j}\,|\,V_s\,|\,\varphi_{\alpha i}\rangle\\&b\text{ type: }\ \langle\varphi_{\beta j}\,|\,V_\beta\,|\,\varphi_{\alpha i}^{\vec{R}}\rangle,\quad \alpha\neq\beta\,.\end{aligned} \tag{16}$$

The a-type or crystal-field integrals have both the orbitals on one oxygen site and the potential on a neighboring silicon site, of which there are three lying in a plane as mentioned above. The matrix elements which include these integrals are $\vec{k}$ independent. The b-type integrals have the potential and an orbital on one oxygen site and the other orbital on a second oxygen site. Matrix elements which include this type of integral are $\vec{k}$ dependent. We express both a- and b-type integrals in terms of disposable parameters following Slater and Koster.[1] These parameters are obtained by properly scaling the parameters from β-cristobalite.[2]

The a-type integrals do not appear in the Hamiltonian matrix H in the usual CP scheme.[5,6] This is valid only if the CP equation is used to obtain the basis orbitals, and is invalid in general if the basis orbitals are chosen to be of atomic symmetry. The a-type integrals should be nonzero for atomiclike basis orbitals unless they vanish identically due to the symmetry of the lattice. In this regard our CP equation [Eq. (6)] is better since it, at least, preserves the symmetry of the orbitals as atomiclike, and the a-type integrals are properly accounted for.

V. THE VALENCE BAND

We treat the O $2s$ and $2p$ bands separately. This is, again, in the spirit of an ionic model and is a good approximation if we consider the large energy difference of the two bands. The relevant matrices to be diagonalized are, therefore, reduced in size. This is very convenient in the case of an empirical tight-binding study where one looks for analytic expressions for energy eigenvalues in terms of the parameters at the high-symmetry points in the Brillouin zone.

For the O $2s$ band we have a 4×4 matrix to be diagonalized:

$$\begin{aligned}H_{\beta s,\alpha s}={}&\left[E_s+\left\langle\varphi_{\alpha s}\,\middle|\,\sum V_s\,\middle|\,\varphi_{\alpha s}\right\rangle\right]\delta_{\alpha\beta}\\&+\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)}\langle\varphi_{\beta s}\,|\,V_\beta\,|\,\varphi_{\alpha s}^{\vec{R}}\rangle(1-\delta_{\alpha\beta}),\quad |\vec{R}+\vec{d}_\alpha-\vec{d}_\beta|<c,\quad \alpha,\beta=3,4,5,6\,.\end{aligned} \tag{17}$$

(The subscript s refers to O $2s$ orbitals in $|\varphi_{\alpha s}\rangle$ and E_s, and a silicon potential center in V_s.) All the diagonal elements have the same value which is given by

$$A=E_s+\langle\varphi_{\alpha s}\,|\,\sum_s V_s\,|\,\varphi_{\alpha s}\rangle\ ,\quad \alpha=3,4,5,6 \tag{18}$$

$$A=E_s+\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle+2\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle'\ . \tag{19}$$

$\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle$ has the O-Si distance 1.810 Å and $\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle'$ has the O-Si distance 1.757 Å. The parameter A does not have $\vec{k}$ dependence and defines only the position of the band. Among the off-diagonal elements there are two different b-type parameters, D_1 and D_2:

$$D_1=\langle\varphi_{\beta s}\,|\,V_\beta\,|\,\varphi_{\alpha s}^{\vec{R}}\rangle,\quad\text{for }|\vec{R}+\vec{d}_\alpha-\vec{d}_\beta|=2.289\ , \tag{20}$$

$$D_2=\langle\varphi_{\beta s}\,|\,V_\beta\,|\,\varphi_{\alpha s}^{\vec{R}}\rangle,\quad\text{for }|\vec{R}+\vec{d}_\alpha-\vec{d}_\beta|=2.522\ , \tag{21}$$

in angstrom units. The values of the parameters are obtained by scaling the parameters from β-cristobalite. In β-cristobalite the parameter A has the value

$$E_s+2\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle=-26.67$$

in units of eV, where the two neighboring silicons are 1.612 Å away from the oxygen. Since the structure of the band does not depend on A, we take $A=-26.67$ eV without scaling it. However, any scaling will not change the above value by any appreciable amount because

$$|E_s|\gg|\langle\varphi_{\alpha s}\,|\,V_s\,|\,\varphi_{\alpha s}\rangle|$$

and the contribution to A from the integrals

TABLE II. The overlaps for O 2s and O 2p orbitals for various separation distances in β-cristobalite and stishovite. The overlaps are obtained using atomic orbitals (Ref. 24).

	O-O separation (Å)	s overlap	p_σ overlap	p_π overlap
β-cristobalite	2.630	0.008 05	−0.017 88	0.002 37
stishovite	2.289	0.021 29	−0.043 55	0.007 04
	2.522	0.011 02	−0.023 90	0.003 36

$\langle \varphi_{\alpha s} \mid V_s \mid \varphi_{\alpha s} \rangle$ is very small. For β-cristobalite there is only one b-type parameter $\langle \varphi_{\beta s} \mid V_\beta \mid \varphi_{\alpha s}^{\vec{R}} \rangle = -0.214$ eV with $|\vec{R} + \vec{d}_\alpha - \vec{d}_\beta| = 2.630$ Å. D_1 and D_2 are obtained from this as proportional to the overlaps between the two O 2s orbitals, which we find using[24] STO's (Table II). The resulting values are $D_1 = -0.5659$ eV and $D_2 = -0.2929$ eV.

These values are then used to generate the O 2s valence band throughout the Brillouin zone. The density of states is also calculated. The results are shown in Fig. 3. They look similar to those obtained by Robertson for SnO_2.[17] The doubly degenerate bands in our calculation do not have any dispersion except from the symmetry point X to R along the line W, in contrast to those obtained by Robertson for SnO_2. This is probably because we neglect interactions beyond nearest neighbors (<2.665 Å). The width of the O 2s band is about 4.5 eV, which is almost twice those of α-quartz and β-cristobalite.

In the case of the O 2p valence band the relevant 12×12 matrix has elements

$$H_{\beta j,\alpha i}(\vec{k}) = E_i \delta_{\alpha\beta}\delta_{ij} + \left\langle \varphi_{\alpha j} \,\middle|\, \sum V_s \,\middle|\, \varphi_{\alpha i} \right\rangle \delta_{\alpha\beta} + \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{d}_\alpha-\vec{d}_\beta)} \langle \varphi_{\beta j} \mid V_\beta \mid \varphi_{\alpha i}^{\vec{R}} \rangle (1-\delta_{\alpha\beta}), \quad |\vec{R}+\vec{d}_\alpha-\vec{d}_\beta| < c \; . \tag{22}$$

The two center a- and b-type integrals are evaluated following Slater and Koster,[1] expressing a p orbital as a linear combination of P_σ and $P_{\pi^\pm}$ functions along and perpendicular to a vector connecting the two centers concerned. The integrals thus reduce to eight disposable parameters, four of them a-type and the other four b-type:

$$(pp\sigma)_a,\ (pp\pi)_a,\ (pp\sigma)'_a,\ (pp\pi)'_a \ ,$$

$$(pp\sigma)_b,\ (pp\pi)_b,\ (pp\sigma)'_b,\ (pp\pi)'_b \ .$$

Unprimed and primed notations denote for a-type the distances 1.810 and 1.757 Å between the Si and O, respectively. For b-type the primed and unprimed parameters have the two O centers 2.289 and 2.522 Å apart, respectively.

Unlike the case of the O 2s band, the a-type integrals contribute to the off-diagonal elements and their contributions to all the diagonal elements are no longer identical. Thus they contribute to both the structure and the position of the band. However, it can be shown that the structure of the band depends only on the differences $[(pp\sigma)_a - (pp\pi)_a$ and $(pp\sigma)'_a - (pp\pi)'_a]$; $(pp\pi)_a$ and $(pp\pi)'_a$ merely define the position of the band. Since we are not concerned with the position of the band, we consider the parameters $(pp\pi)_a$ and $(pp\pi)'_a$ to be zero. Therefore, the structure of the band is described by six parameters:

$$(pp\sigma)_a,\ (pp\sigma)'_a \ ,$$

$$(pp\sigma)_b,\ (pp\pi)_b,\ (pp\sigma)'_b,\ (pp\pi)'_b \ .$$

The value of E_i can be adjusted to define the zero of the energy at the top of the valence band.

To obtain realistic values of the parameters we use, as before, the results from β-cristobalite, obtained by a similar tight-binding fit to a detailed band-structure calculation. In β-cristobalite $(pp\sigma)_a = -2.25$ eV, $(pp\sigma)_b = 0.9$ eV, and $(pp\pi)_b$ is neglected. We scale our a-type parameters from the above value as proportional to the inverse of the Si-O distances. To obtain the values for b-type parameters, scaling is done as proportional to the overlap between the O 2p orbitals. As in the case of β-cristobalite we neglect $(pp\pi)_b$ and $(pp\pi)'_b$ and use the values of the parameters as mentioned above (Table III). Although the p_π overlap is not totally negligible compared to the p_σ overlap, we find that small values of the parameters $(pp\pi)_b$

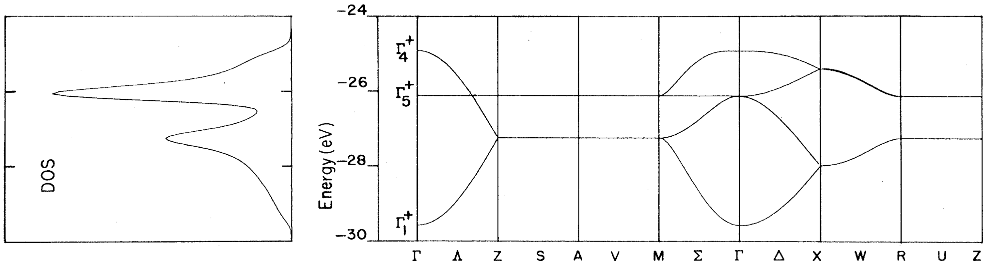

FIG. 3. Computed O 2s energy-band structure and density of states (DOS) of stishovite.

TABLE III. The tight-binding parameters for the p band of stishovite, in units of eV.

$(pp\sigma)_a = -2.0038$

$(pp\pi)_a = -0.0$

$(pp\sigma)'_a = -2.0643$

$(pp\pi)'_a = -0.0$

$(pp\sigma)_b = \ \ 2.1921$

$(pp\pi)_b = -0.0$

$(pp\sigma)'_b = \ \ 1.2030$

$(pp\pi)'_b = -0.0$

and $(pp\pi)'_b$ do not change the structure of the top of the valence band. The density of states is also calculated sampling 550 points of the irreducible Brillouin zone. The results are shown in Fig. 4.

The results of our simple calculation agree quite well with the results for other dioxides of group-IV elements having the rutile structure. The top of the valence band is of Γ_3^+ symmetry, as found experimentally for other oxides mentioned above by various authors and also by Robertson using a detailed calculation.[16,17] Also, our density of states looks somewhat similar to that obtained by Robertson for SnO_2; exact agreement would not be expected since we are dealing with two different substances.

The p-band width for stishovite is about 12.5 eV, compared to 11.5 eV for α-quartz and 9.5 eV for β-cristobalite. The p band does not have any gap such as is present in the case of both α-quartz and β-cristobalite.

According to our ionic model for stishovite the bottom of the conduction band is composed of Si 3s orbitals, and it will split into Γ_1^+ and Γ_4^+ at $\vec{k}=0$. Γ_1^+ is totally symmetric and should lie below Γ_4^+. Since the transition $\Gamma_3^+ \rightarrow \Gamma_1^+$ is forbidden, the optical edge of stishovite is then direct and forbidden.

VI. CONCLUSION

The valence bands of the rutile-type dioxides of group-IV elements can be described quite well by the anion 2s and 2p orbitals. Previous attempts to obtain such band structures[25] did not give good results because the crystal-field terms were not included in the calculations. In the case of semiquantitative tight-binding studies the crystal-field terms are often neglected, the stated or implied justification being the CP approach of Anderson[5] and Bullett.[6] We use a modified CP equation to include the crystal-field terms and obtain good results. The top of the valence band is found to be of Γ_3^+ symmetry, yielding a direct forbidden optical edge for stishovite.

The valence band of stishovite can be compared with those of α-quartz and β-cristobalite which are also obtained by the same method. The p band of stishovite does not contain any gap, whereas gaps are present in the p bands of the other two polymorphs of SiO_2. The gap in the p band appears to be an effect of the twofold-coordinated oxygen. In the case of a model of amorphous SiO_2 which contains only twofold-coordinated oxygens, this gap in the density of states tends to persist and is bridged by highly localized states.[26] Substances such as oxides,[17] fluorides,[17] and nitrides[27] which have threefold-coordinated anions generally appear to have no gap in the valence band.

The widths of both the s and the p bands of stishovite are larger than those of α-quartz and β-cristobalite. The widths depend on the number of oxygen neighbors of an oxygen atom and in the case of the p band also on the coordination of the oxygen atom. These effects on the width are much stronger for the s band than for the p

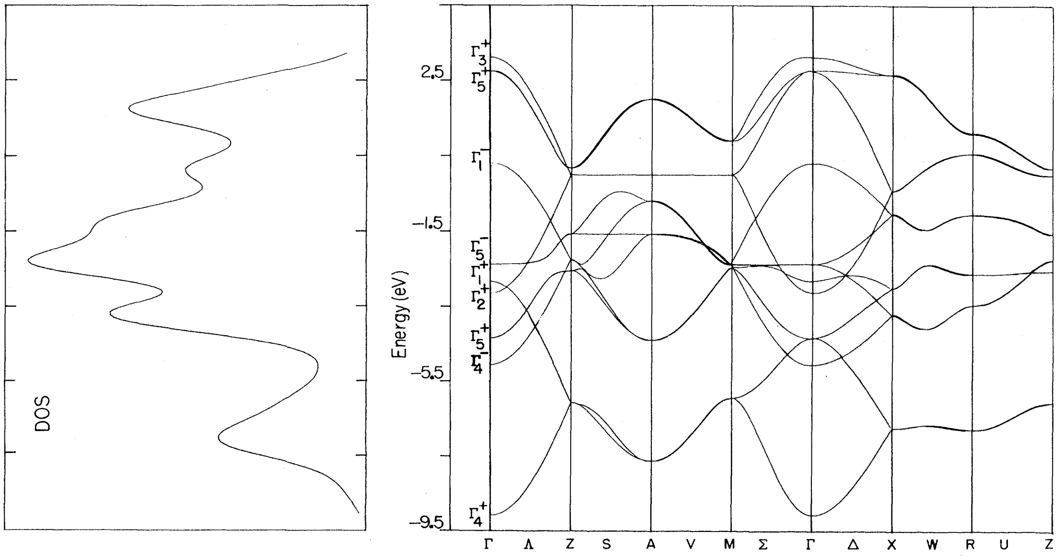

FIG. 4. Computed O 2p energy-band structure and density of states (DOS) of stishovite.

band because of the quite different natures of the *s*-*s* and *p*-*p* interactions. The *s*-*s* interaction does not depend on the structure of the lattice and it is of "additive" nature due to the spherical symmetry of the *s* orbital, while the *p*-*p* interaction has some "cancellation effects" due to its directional nature. For this reason, the width of the upper valence band does not change much as we go from one polymorph of SiO_2 to another.

Thus in extrapolating these results to *a*-SiO_2 we anticipate, as others have, that the overall *p*-band widths of amorphous and crystalline SiO_2 will be about the same. Our observations on threefold- versus twofold-coordinated oxygen lead us to suggest that real *a*-SiO_2, which *will* contain some threefold-coordinated oxygens, will have states in the valence-band gap. These states may merge into bands if the fraction of threefold-coordinated oxygens is large enough. They may also play a role in the transport of "hot" holes, e.g., holes which originate from the lower "bonding" *p* valence band.[28] Thus we feel that detailed studies of the electronic properties of stishovite can play an important role in understanding certain properties of *a*-SiO_2.

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