held for Fermi-surface measurements, such as V_3Si, V_3Ga, and Nb_3Sn. Measurements on other layer compounds should also be very interesting, to study further the effects of the Fermi surface and charge-density wave on one another.

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Band Structure and Optical Properties of Silicon Dioxide*

Philip M. Schneider† and W. Beall Fowler
Physics Department, Lehigh University, Bethlehem, Pennsylvania 18015

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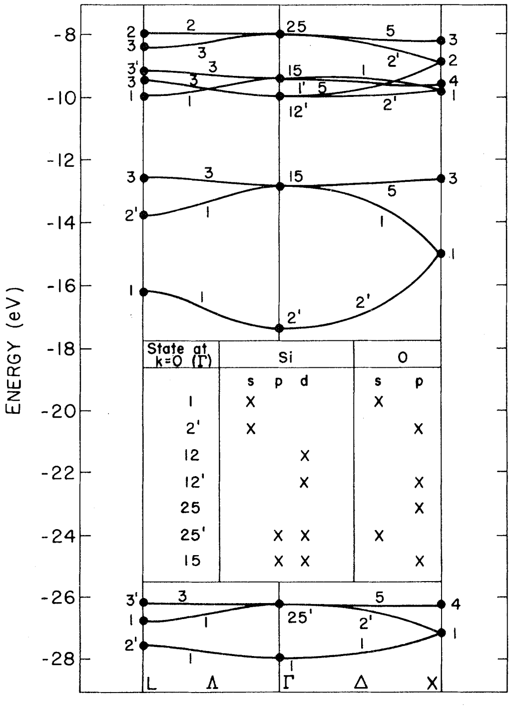
The mixed-basis method has been used to compute the energy bands of an idealized β-cristobalite form of silicon dioxide. A direct-forbidden optical-absorption edge is predicted. Peaks in observed x-ray emission and optical-absorption spectra identified with critical points in the densities of states.

We report the results of mixed-basis calculations of the energy bands of silicon dioxide in the form of idealized β-cristobalite, a diamond structure with an oxygen lying midway between each pair of nearest-neighbor silicons.[1] This is the first detailed band-structure calculation for any form of SiO_2, and complements earlier molecular-cluster calculations[2,3] and semiempirical calculations[4] of the valence bands. Many properties of SiO_2 do not appear to depend strongly on long-range symmetry, as, for example, the optical reflectivity spectrum[5,6] from 8 to 20 eV and x-ray-emission spectra.[7] Consequently, our results provide considerable insight into the analyses of experiments on various forms.

The mixed-basis method[8] utilizes Bloch sums of nonoverlapping[9] atomiclike functions, and symmetrized combinations of plane waves. The crystal potential was taken as a sum of atomic silicon and oxygen potentials, obtained by solving the atomic Hartree-Fock-Slater equations.[10] No adjustable parameters or artificial muffin-tin potentials, difficult to justify[11] in an open solid such as SiO_2, were required. CDC computers at Lehigh University and at Brookhaven National Laboratory were used.

Calculations are reported for the points Γ, X, and L of the first Brillouin zone.[12] The largest matrix diagonalized was 70 × 70 (60 × 60 at Γ). This appeared to yield convergence to within 0.2 eV for all points. Convergence curves and an analysis of other possible numerical errors will be reported elsewhere.

Figures 1 and 2 show the valence and conduction bands, respectively. Our valence bands are somewhat similar to those obtained semiempirically by Pantelides and Harrison.[4] The points actually calculated are shown as dots, with the exception that the top-most valence bands (Γ_{25}, Γ_{15}, Γ_{12}') have been rigidly shifted down by 2.0 eV from the computed values, as seems necessary for a consistent interpretation of the experimental data discussed below in connection with Fig. 3. Possible reasons why these bands turned out to be too high will be discussed elsewhere. The inset to Fig. 1 relates states at Γ to the corresponding atomic states. Similar tables for other symmetry points may be generated from compatibility relations.



State at k=0 (Γ)	Si			O	
	s	p	d	s	p
1	X			X	
2'	X				X
12			X		
12'			X		X
25					X
25'		X	X	X	
15		X	X		X

FIG. 1. The valence bands of ideal β-cristobalite. Computed points are indicated by dots. The top set of bands has been shifted down from the computed values by 2.0 eV. The inset indicates by "X" which atomic functions may be involved in the states at $\vec{k}=0$. The energy scale is defined so that the bottom of the conduction band is at zero.

The highest valence bands, clustered around − 9 eV, are derived from the oxygen lone-pair orbitals,[2,3] oxygen p states oriented perpendicular to the Si-O-Si axis. We estimate that the heavy-hole mass at the top of the band is greater than $10m_e$. The light-hole mass may be $\sim 3m_e$ to $10m_e$. The next set of bands, from ~ − 12 to − 17 eV, represents the Si-O bonding states. They involve mostly silicon s orbitals and oxygen and silicon p orbitals pointing along the Si-O-Si axes. Finally, the ~ 2 eV wide bands around − 27 eV are derived mostly from oxygen 2s; a two-parameter tight-binding fit was made to the seven computed points of these bands, with excellent results, and intermediate points and a density of states were obtained.[13]

Figure 3 indicates a comparison with experimental[14] x-ray-emission spectra. Although not shown here, photoemission results[3] also agree

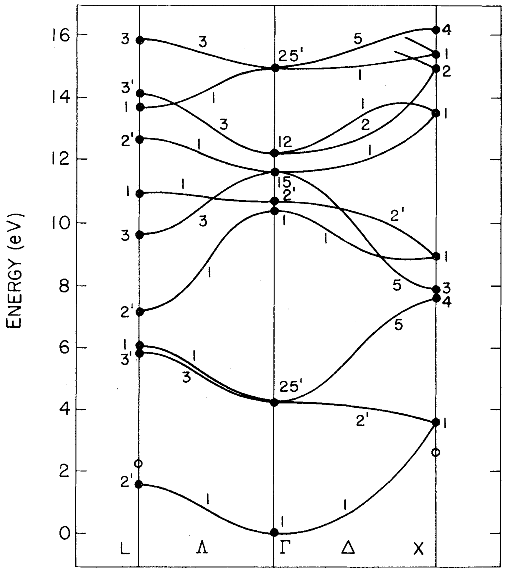


FIG. 2. The lowest conduction bands of ideal β-cristobalite. Computed points are indicated by dots. Open circles at L and X indicate where free-electron bands would intersect these points. The zero of energy is defined as the bottom of the conduction band.

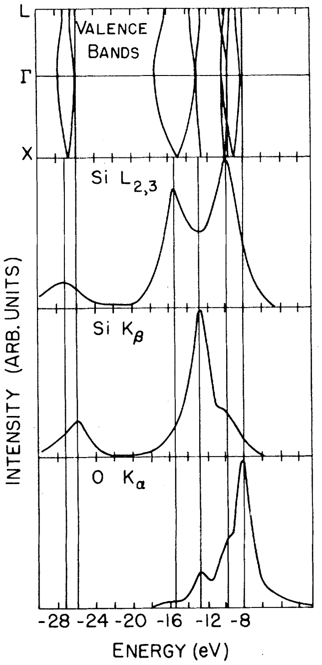


FIG. 3. Comparison of experimental x-ray-emission spectra with the β-cristobalite valence bands (see text, Ref. 14, and Fig. 1 for details). The energy scale is that used in Fig. 1.

well with our calculations. For this comparison, information from group-theoretical selection rules, the atomic nature of wave functions associated with electric-dipole-allowed transitions, and densities of states were combined. For example, transitions from every calculated point in the valence bands are allowed as part of the oxygen $K\alpha$ spectrum. However, the most significant transitions will involve a high density of oxygen p states in the valence wave function. Such will occur[4] at around -13 eV (the relatively flat bonding band involving Γ_{15}), and throughout the upper valence bands at around -9 eV. This appears to be in good agreement with the observed oxygen $K\alpha$ spectrum. One indication that the oxygen lone-pair valence bands must lie approximately as shown is the large density of oxygen p states in the topmost (Γ_{25}) band; much of the strongest peak in the oxygen $K\alpha$ spectrum must originate from this band. Further adjustment of the lone-pair bands relative to each other could yield better agreement with the spectra. We choose to present the computed bands here, largely because the bending of the Si-O-Si bond could account for much of the correction. It is, however, likely that the long tails in the observed spectra arise from instrumental broadening or from structural disorder.[15]

Our valence bands are also consistent with the Si $K\beta$ and $L_{2,3}$ emission bands. $L_{2,3}$ samples silicon s and d character; relatively large densities of such states will occur around L_2' in the lowest oxygen s band, L_1 in the bonding bands, and througout the Γ_{15} and Γ_{12}' lone-pair bands (but not within the Γ_{25} lone-pair band). $K\beta$ samples silicon p character, which occurs in the upper oxygen s band, the upper Γ_{15} bonding band, and the lower lone-pair bands (again, not within the Γ_{25} band). Peaks and bumps in the observed spectra are in general agreement with these assignments. Gilbert *et al.*,[16] have noted that the silicon wave-function coefficients involved in these transitions are relatively small; they computed only 4% Si $3p$ character in the state leading to the lower-energy $K\beta$ band. Thus the Si $3d$ admixed into Γ_{15} and Γ_{12}' does not necessarily imply strong $p\pi$-$d\pi$ bonding.

The lowest conduction-band minimum is at Γ_1, and it is rather free-electron-like. This is similar to a tight-binding result of Weaire and Thorpe.[13] We have not yet calculated the effective mass at Γ_1, but in analogy with other insulators[17] we conjecture that it will turn out to be $\sim 0.5 m_e$. The separation between Γ_1 and Γ_{25}' is within ~1 eV of the atomic silicon $3s$-$3p$ splitting,[18] and Γ_{12} (which contains silicon $3d$, but no s or p) is within ~2 eV of the atomic $3d$ position with respect to $3s$ and $3p$. Clearly there is a good deal of admixture, and some of the bands are also associated with oxygen $3s$, $3p$, $3d$. We will not analyze the higher bands in any further detail at this time.

The computed band gap (with the shifted upper valence bands) is 8.0 eV, as compared with a value 8.9 eV obtained by photoconductivity measurements.[19] The lowest-energy optical edge, from Γ_{25} to Γ_1, is direct but forbidden; a direct allowed edge occurs about 1.5 eV higher in energy, from Γ_{15} to Γ_1. This result is likely to be approximately preserved[20] even in amorphous SiO_2, since it arises from a transition between fairly localized oxygen $2p$ and silicon $3s$ states. A careful measurement of the optical-absorption edge should yield the characteristic $(\hbar\omega - E_g)^{3/2}$ behavior,[21] unless the disorder seriously alters the optical selection rules.

The optical-reflectivity spectrum[5] of SiO_2 has characteristic peaks at 10.3, 12.0, 14.4, and 17.2 eV. The 12-eV peak in some cases has resolved structure.[5,6] By combining selection rules and regions of expected high densities of states, we suggest that the first two peaks involve the lowest L_2' as the final state; for the first peak, the initial state is L_3 in the upper valence band, and for the second peak the initial states are L_3 and L_1 in the lower part of the oxygen lone-pair band.

The peak at 14.4 eV probably involves the first Γ_{25}' conduction band in the final state. It is most likely due to $L_2 \rightarrow L_3'$, although others are allowed; probably some unresolved structure exists here. The 17.2-eV peak could involve either (or both) valence L_3 to the L_2' at ~7 eV; other possibilities are from L_1 to the lowest L_3', or L_3' to L_1. Clearly, as one goes to higher photon energies the possibilites increase.

We will discuss in subsequent papers the analysis of electron-energy-loss[22] and x-ray-absorption[23] data. All of the high-state-density regions of the lower conduction bands are optically accessible by electric dipole transitions from the Si 1*s* and 2*p* and oxygen 1*s* states, but core-exciton effects[4] may considerably complicate the picture.

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