

Energy Bands and the Soft-X-Ray Absorption in Si[†]

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The contribution of transitions from the L shell to the imaginary part of the dielectric constant of silicon has been calculated including one-electron matrix elements. The inclusion of one-electron matrix elements does not resolve the discrepancy found between conduction-band density of states and soft-x-ray spectra. It is pointed out that, contrary to the claim of Kunz, the soft-x-ray data do not tell us the order of the zone-center levels in Si.

In a recent letter, Kunz¹ suggested that a new model for the energy-band structure of Si was required to agree with the soft-x-ray data.² In the proposed model, Γ'_2 would be below Γ_{15} . We take strong exception to the manner in which this inference is drawn. The essential feature of the models Kunz puts forward is not the order of Γ'_2 and Γ_{15} , but the placement of these levels. Both of these levels have been positioned to enhance the low-energy conduction-band density of states. However, the placement of these levels in his model is inconsistent with optical data. As has been previously suggested,² simple one-electron states may not be appropriate for the quantitative interpretation of x-ray absorption. We do find that inclusion of calculated one-electron matrix elements makes no consequential difference, which is in agreement with the assumption of Kunz.

The soft-x-ray absorption spectrum of Si rises much more abruptly near the onset of transitions from the $L_{II,III}$ shell than does the Si conduction-band density of states. Kunz argues that a model in which Γ'_2 is below Γ_{15} would produce a joint density of states for these x-ray transitions more in agreement with experiment. However, the order of Γ'_2 and Γ_{15} is not the crucial distinction between his models a and b and the models of Brust³ or Cohen and Bergstresser.⁴ The key difference is the placement by Kunz of those levels at 2.2 and 2.4 eV above Γ'_{25} . This placement yields a conduction band more like that found by Stukel and Euwema⁵ or Chaney, Lin, and Lafon.⁶ Perhaps it should be noted that neither of these works^{5,6} attempts a reconciliation between their calculation and experiment in regard to these zone-center levels. For these levels, they only compare with other theoretical work. Obviously, the low-energy conduction-band density of states is augmented if the zone-center levels are thusly lowered with respect to the bottom of the conduction band. However, placing those levels below about 3.2 eV above Γ'_{25} is inconsistent with optical data.⁷ The direct threshold in Si is about 3.2 eV. If either Γ'_2 or Γ_{15} were below that energy, the allowed transition to that state from Γ'_{25} would be detectable in differential spectroscopy. Such

transitions have never been reported.⁷

In an attempt to reconcile the x-ray data and the theoretical spectrum, we have calculated the inter-band matrix elements coupling the Si $2p$ states to the conduction-band states and included them in an ϵ_2 and absorption-coefficient calculation. The conduction-band wave functions were expanded in orthogonalized plane waves employing a simple crystal-potential model based on overlapping atomic potentials calculated using the Kohn-Sham exchange approximation.⁸ Following Kunz, a spin splitting of 0.70 eV for the $2p$ level is included, but otherwise spin-orbit (and other relativistic) effects are neglected. The joint density of states for transition from the $2p$ core levels to the conduction band is shown in Fig. 1 for the model we use. The joint density of states is very similar to that which Kunz shows for the Brust or Cohen and Bergstresser models. In Fig. 2 we show the transition probability $E^2 \epsilon_2$ calculated, including one-electron matrix elements.⁹ It is apparent that for the final states of interest the magnitudes of the calculated one-electron matrix elements are sufficiently constant, and that the conclusions reached assuming constant

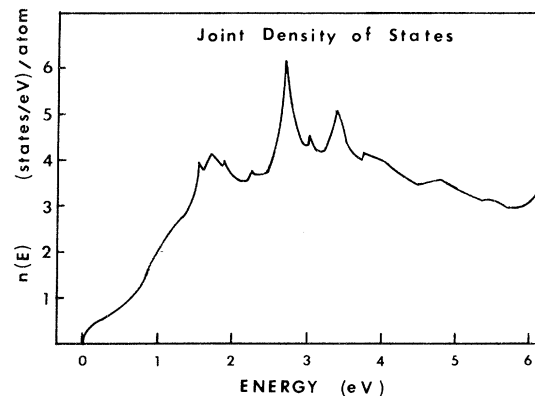


FIG. 1. Joint density of states for x-ray transition from the Si $2p$ core states to the conduction band. The energy is measured from the bottom of the conduction band.

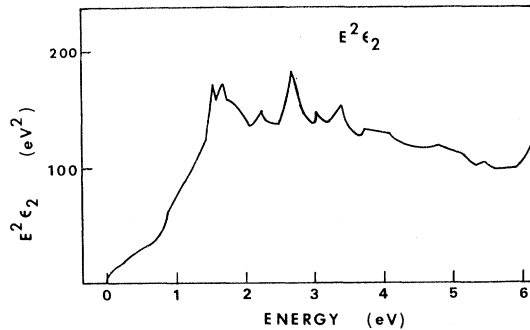


FIG. 2. Transition probability $E^2\epsilon_2$ for x-ray transitions from the Si $2p$ core states to the conduction band. Calculated one-electron matrix elements are included. The absorption coefficient in cm^{-1} can be found by multiplying the scale by 506, assuming the transition energy is 100 eV and the real part of the dielectric constant equal to 1.0.

matrix elements are unchanged. Note that we have an absolute scale on both the joint density of states and $E^2\epsilon_2$. The essential difference between these figures is a velocity matrix element \bar{v} , whose average squared magnitude is such that $m_0\bar{v}$ is about 0.13 a. u. Ignoring the variation in real part of the dielectric constant and the transition energy, $E^2\epsilon_2$ is proportional to the absorption coefficient. Assuming the absorption coefficient to be zero below threshold, we find the value at the first peak to be about $0.9 \times 10^5 \text{ cm}^{-1}$, which is about the same magnitude as the increase found experimentally.² As would be expected, Γ'_2 was more strongly coupled to the $2p$ level than was the Γ_{15} state,¹⁰ but the magnitudes of the matrix elements along the Δ axis (which is where the conduction-band minimum is located) were relatively constant. The effect of one-electron matrix elements does not shift the peak by even 0.1 eV. Except near Γ_{15} , all of the low-energy conduction band seems to have enough s character to be fairly uniformly coupled by the dipole operator to the $2p$ core level.

Finally, should soft-x-ray spectra be expected to agree quantitatively with the one-electron joint density of states? Kunz points to the alkali halides^{11,12} and says "yes." We have strong doubts. It is a reasonable assumption that for x-ray excitations the core hole will be quite localized. In such a case, it seems necessary to consider the possibility that the final state of the system might find

the electron not in a band state uniformly distributed throughout the crystal, but in a state in which there is a distinct localization of the electron about the atom on which the hole is located. In such a state one expects the electron-hole Coulomb interaction to lower the energy, and hence to enhance the leading edge transition probability; this is similar to what is calculated to describe¹³ excitonic enhancement in terms of unbound hydrogenic states.

For the alkali halides,^{11,12,14,15} we note a systematic difference between x-ray transition from the cation and anion. The lowest conduction bands in alkali halides are predominantly alkali bands. When the x-ray transition originates from a halide core state, Kunz finds excellent agreement between theory (joint density of states) and experiment (optical density). (The agreement is qualitative; he does not make an absolute comparison.) The agreement is much less spectacular, for the few cases he shows, when the transition originates in an alkali core state. In the latter case, the first experimental peak is always larger relative to the remainder of the spectrum than theory predicts. (For example, see Figs. 5 and 6 of Ref. 11 for transitions from the Li K shell to a Li conduction band of LiCl.) We suggest that this is precisely a Coulombic enhancement of the leading edge.

Cardona *et al.*¹⁶ do find reasonable agreement between unenhanced theory and experiment for InAs for x-ray transitions from the In d band. However, there is an important difference between InAs and Si. The matrix element for the transition to the bottom of the conduction band in InAs should be very small. Whereas the InAs transitions originate in d states, they are not coupled to the s character of the conduction band. The transition to Γ_1 is not actually symmetry forbidden in that plane-wave f character can couple to d , but the threshold state certainly has predominately s character in the region of overlap with the core. This may be sufficient to wash out any enhancement effects.

In disagreement with Kunz, we feel the transition probability in x-ray transitions is not well enough understood theoretically to reject the evidence from optical data in interpreting the band structure of a semiconductor such as Si. Further, we would suggest, on the basis of the Si evidence, that interpretation of less well-known band structures on the basis of primarily x-ray data should be done very cautiously. We agree with Gähwiller and Brown² that the problem needs further theoretical study.

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⁸This same model has recently been employed to study matrix elements in optical transitions. It was selected for its simplicity, but yields energy levels for important optical transitions within a few tenths of an eV of where we would choose them [see J. P. Van Dyke, Phys. Rev. B **5**, 1489 (1972)].

⁹The zonal integration procedure is the same as that employed in Ref. 8. The OPW calculation is interpolated by parameterless $\vec{k} \cdot \vec{p}$ from six points in the Brillouin zone. However, since core bands are not readily incorporated in the $\vec{k} \cdot \vec{p}$ expansion [see J. P. Van Dyke, Phys. Rev. B **4**, 3375 (1971)], the core eigenvalues are assumed independent of k and only the matrix elements interpolated. This means for core-conduction-band matrix elements the quantity actually being used is $\langle \Phi_{\text{core}}(\vec{k}) | e^{-i(\vec{k}-\vec{k}_0) \cdot \vec{r}} | \Phi_{\text{conduction}}(\vec{k}) \rangle$ where we want the matrix element without the exponential (k_0 is the point of $\vec{k} \cdot \vec{p}$

expansion). We considered this error by using less than six OPW points as well as by comparing matrix elements at points in the zone as found from different $\vec{k} \cdot \vec{p}$ expansion points and concluded that it was not significant enough to warrant adding additional OPW points or expanding the exponential as was done by J. Klima [J. Phys. C **3**, 70 (1970)].

¹⁰Contrary to the assertion of Ref. 2, the transition is not forbidden at zone center to Γ_{15} . In the diamond structure the Γ_{15} symmetry admits d character as well as p character about the atomic site.

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Experimental Verification of the Surface Quantization of an n -Type Inversion Layer of Silicon at 300 and 77° K

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The quantization of the motion, perpendicular to the surface, of electrons in an inversion layer at the surface of a silicon substrate is experimentally verified by accurate capacitance measurements at 77 and 300°K. From the measurements the average distance of the electrons from the interface can be derived. To obtain agreement with the calculated value, the quantization has to be taken into account.

The electrons in an inversion layer at the surface of a p -type semiconductor are bound to the surface in a potential well caused by an externally applied electric field normal to the surface. The electron motion normal to the surface is therefore quantized.¹ Each energy level causes a two-dimensional subband, with the electron motion parallel to the surface being free. This quantization has been demonstrated at temperatures below 4.2°K, by a number of experiments.²⁻⁶ In this paper it is shown that quantization effects can also be measured up to room temperature by accurate capacitance measurements between the gate and the short-circuited source, drain, and bulk contacts of a metal-oxide-silicon-semiconductor transistor (MOST).

In the effective-mass approximation the electron motion in the z direction perpendicular to the surface is determined by Schrödinger's and Poisson's equation^{7,8}

$$\left(-\frac{\hbar^2}{2m_x^j} \frac{d^2}{dz^2} - qV(z)\right) \psi_i^j(z) = E_i^j \psi_i^j(z), \quad (1)$$

$$\frac{d^2 V}{dz^2} = \frac{q}{\epsilon} \left(N_A + \sum_{i,j} N_i^j |\psi_i^j(z)|^2\right). \quad (2)$$

E_i^j is the i th energy level of the electrons in valley j of the conduction band with effective mass m_x^j in the z direction. For a silicon (100) surface, we have two valleys with $m_x = 0.98m_0$ and four with $m_x = 0.19m_0$.⁷

The space-charge density in Poisson's equation