Now, the θ-dependent part in the molecular interaction of the cholesteric phase is expressed by

$$V_{ab} = \langle \sum_j V_{ij}{}^{pp} \rangle + \langle \sum_j (V_{ij}{}^{pq} + V_{ij}{}^{qp}) \rangle + V_{ab}{}^{qq} \tag{4}$$

$$= -(\alpha \cos 2\theta + \frac{2\beta}{r_{ab}} \sin 2\theta + \frac{\gamma}{r_{ab}^2} \cos 2\theta) \frac{3\pi}{8(r_{ab})^4}, \tag{5}$$

where α is related to the anisotropy of the molecular polarizability and β, γ are related to anisotropy of the molecule. By minimizing V with respect to θ, the stable twist angle θ is given by

$$2\theta \simeq \tan 2\theta = \frac{2\beta}{\alpha r_{ab} + \gamma/r_{ab}}. \tag{6}$$

In nematic-cholesteric mixtures, the first, second, and third terms on the right-hand side of Eq. (4) are proportional to N, n, and n^2/N, respectively. Then, the substitution of n/N by C_1 in the formula (6) leads to the expression

$$\theta = BC_1/(1 + AC_1^2),$$

where

$$A = \gamma/\alpha r_{ab}^2, \quad B = \beta/\alpha r_{ab}.$$

The experimental result is well explained with just the terms mentioned above.

The cholesteric helical structure will probably depend on the weak dispersion forces given by the second-order perturbation of not only the dipole-dipole and the dipole-quadrupole interactions but also the quadrupole-quadrupole interaction.

Finally, it should be emphasized that the curve of helical twisting power versus concentration has a maximum value in nematic (MBA)-cholesteric (CP) mixtures and that it is quite useful for understanding the helical ordering of cholesterics.

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

A. Barry Kunz
Department of Physics and Materials Research Laboratory, University of
Illinois at Urbana-Champaign, Urbana, Illinois 60801

The soft-x-ray absorption spectrum from the Si $L_{II,III}$ shell is used to study several energy-band models for Si. The calculations are based on the empirical pseudopotential method. The results support the recent Si band model obtained by Stukel, Euwema, and Chaney, Lin, and Lafon. We suggest that the $\Gamma_{2'}$ level lies below Γ_{15} in the Si conduction band.

Silicon has a unique place in solid state physics. It forms a basis for much of our advanced solid-state electronics industry and is probably one of the most studied materials in existence. Silicon has been the subject of numerous band-structure calculations by orthogonalized plane-wave,[1] $\vec{K} \cdot \vec{P}$,[2] pseudopotential,[3] and tight-binding[4] methods. Nonetheless, the agreement between theory and
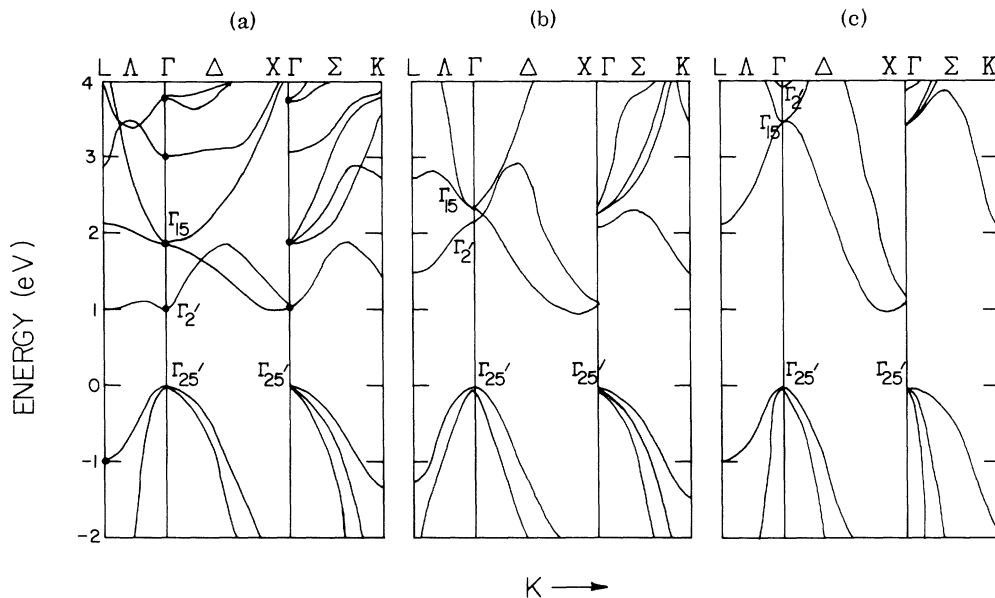
FIG. 1. Energy bands for Si computed by the empirical pseudopotential model, for three choices of pseudopotential. In case (a) we match the Si bands to a Ge-type structure, in (b) we match closely the bands of Refs. 4 and 5, and in (c) we use the potential of Cohen and Bergstresser, Ref. 3.

experiment in terms of understanding the optical properties is less than good. In general, recent band calculations[4,5] yield features which are not in agreement with older work.[1-3] In this paper we examine the soft–x-ray spectroscopy of Si[6] and we find that the experimental comparisons favor the more recent calculations.

In studying the soft–x-ray data we limit our problem essentially to the structure of the conduction band since the ground state in question is the $L_{II,III}$ (i.e., the spin-orbit–split Si $2p$ state) and this state is deep and flat. The splitting between the L_{II} and L_{III} levels is 0.695 eV[7] and is due to spin-orbit effects. The essential difference between silicon band structures involves the relative position of the $\Gamma_{2'}$ and Γ_{15} conduction-band states at the center of the zone and the associated differences throughout the first Brillouin zone. The more recent calculations find that the $\Gamma_{2'}$ level lies below the Γ_{15} level.

In this paper we discuss the following calculation. We model the silicon band structure using an empirical pseudopotential. The band models we chose are (a) one in which the Si bands resemble those of Ge; (b) bands which closely resemble those of Refs. 4 and 5; (c) bands using the pseudopotential of Cohen and Bergstresser[3] which represents the bands of Refs. 1-3. These energy bands are shown in Fig. 1. Our program reproduced the Cohen-Bergstresser bands in an essentially

exact manner. The bands were computed at 505 equispaced nonequivalent points in the first Brillouin zone and a joint density-of-states histogram was constructed for transitions from the $L_{II,III}$ state to the conduction bands. Here we use a value of 0.7 eV for the spin-orbit splitting of the $L_{II,III}$ shell and we weight these levels 1:2 to take degeneracy into account. We adjust the position of the conduction band relative to the core so that the theoretical onset of absorption coincides with the experimental one.

In Fig. 2 we show the joint density of states computed from band models (a), (b), and (c) above and also that of Brust[3] along with the experimental data of Gähwiller and Brown.[6] Here we show two different experimental results. The first is obtained by performing optical density measurements on an etched thin-film single crystal of Si and the second is obtained by measuring the optical density of an evaporated thin film of polycrystalline Si. In general the etched thin-film data show sharper and more detailed structure and are probably more reliable. There is one essential feature in both experiments and that is the rather steep slope of the initial Si absorption. This edge rises in less than 0.1 eV for the etched sample and in about 0.7 eV for the evaporated film. In general the calculated curves rise much more slowly than the 0.1-eV figure. The germanium-based band model rises most rapidly, and
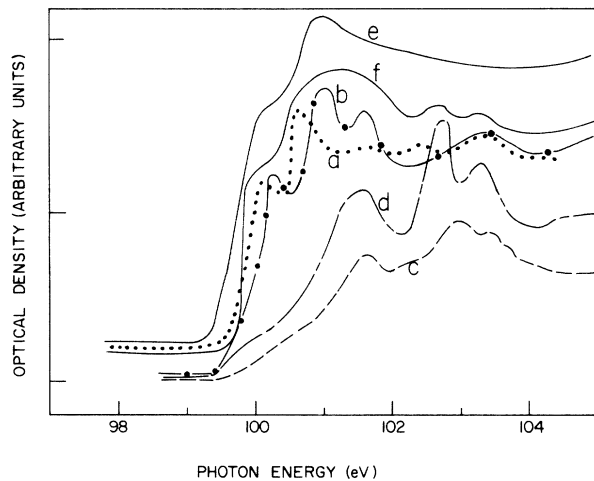
PHOTON ENERGY (eV)

FIG. 2. The joint density of states for transitions from the $L_{II,III}$ shell in Si to the conduction band. Curve a is for a Ge-like band model, curve b for the model of Refs. 4 and 5, curve c for the Cohen-Bergstresser model, Ref. 3, and curve d for the bands of Brust, Ref. 3. Curves e and f are the experimental results of Gähwiller and Brown, Ref. 6. Curve f is for an etched single crystal, and e is for an evaporated polycrystalline sample.

the model from Refs. 4 and 5 also rises rapidly. In the first case the rise is in 0.4 eV and the second in 0.8 eV. These are in fair agreement with the etched-film data and in good agreement with the evaporated-film data. On the other hand the older band models[1-3] produce less good results and rise in 2.0 eV. We find good agreement between our model (c) and that of Brust.[3]

The density of states for the Si conduction band which we produce by our model (b) is found to be in excellent agreement with the result given by Stukel and Euwema.[5] In the case of the newer band model the first maximum is associated with the position of the $\Gamma_{2'}$ conduction band and the accidental degeneracy of the bands along Δ coming from $\Gamma_{2'}$ and Γ_{15}. In the case of the older band models the maximum is associated with the Γ_{15} point.

The author feels that the soft-x-ray data for Si

should be understood in terms of the conduction-band density of states as it is for other semiconductors[8] and for the alkali halides.[9] If this is the case, we argue that the soft-x-ray data favor a band model for Si in which the $\Gamma_{2'}$ point lies below the Γ_{15} point. Such a band model exists[4,5] and effort should be expended in optimizing this model with experiment. We note that such a model in its present form is no less consistent with either optical absorption studies or electroreflectance data than are the older models. We conclude then that the soft-x-ray studies for Si are important and suggest a modification in our thinking as to what the Si band structure is really like.

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