

## Model dielectric function for semiconductors: Si<sup>†</sup>

John T. Foley and Uzi Landman\*

*Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627*

(Received 26 January 1976; revised manuscript received 29 March 1976)

A model dielectric function for semiconductors based on the two-band tight-binding model of Chadi and White is presented. The complex dielectric function includes transitions in the entire frequency range and satisfies the Kramers-Kronig relations and the  $f$ -sum rule. A method of analyzing optical experiments is discussed and applied to Si.

### I. INTRODUCTION

The optical properties of semiconductors and the relation between the observed optical spectra and the electronic structure have been the subject of intensive studies.<sup>1,2</sup> The fact that dielectric response of semiconductors in the visible and uv range originates from direct interband transitions<sup>3</sup> has been utilized for the analysis of the optical reflectivities via the use of the imaginary part  $\epsilon_2$  of the dielectric function which is related to the joint density of states of the valence and conduction bands.<sup>2b,3,4</sup> Detailed calculations provided understanding of the nature of the optical response of the system and in several important cases an assignment of electronic transitions to prominent features of the spectra was achieved. Among these studies, those employing the empirical-pseudo-potential method<sup>2c</sup> and the critical-point analysis<sup>2b</sup> have achieved much popularity.

Another approach to the study of the optical properties of semiconductors is via simple analytical model calculations.<sup>5,6</sup> This approach proved to be useful in analyzing the explicit dependence of the dielectric response of the system on the model parameters, and in forming the basis for the formulation of the theory of bonding and ionicity in  $A^N B^{8-N}$ -type crystals.<sup>7</sup> In addition, some of these models provide a method for the analysis of experimental data. In the analytical-model approach, a model of the electronic structure of the material is constructed or postulated first, and the dielectric function is then derived. It has been recognized that analytical-model dielectric functions which have been proposed, exhibit some deficiencies. Thus, for example, a free-electron model<sup>8</sup> yields a static dielectric function which diverges in the long-wavelength limit,<sup>5,9</sup> and improvements of the nearly-free-electron model<sup>5</sup> lead to dielectric functions which do not satisfy the Kramers-Kronig relation<sup>1</sup> and/or the  $f$ -sum rule.<sup>10,11</sup> In addition, the previous suggested model dielectric functions apply in restricted frequency ranges with limited agreement to experiment.

Our objective in this study, is to construct a model dielectric function in which the above problems are avoided and to apply it to the analysis of experimental data. Our model is based on a local-binding two-band Hamiltonian description of the electronic structure for part of the spectrum (low frequencies), and an approximate form of the random-phase-approximation (RPA) dielectric function for the rest of the spectrum. As will be shown below, the dielectric function which we derive satisfies the Kramers-Kronig relation by construction, it applies to the entire frequency range of measurements, and the consistent procedure for the determination of the model parameters via the analysis of experimental data demands an exact satisfaction of the  $f$ -sum rule and yields results which are in very good agreement with experimental observations. In Sec. II we describe the construction of the dielectric function and derive analytical formulas for the complex dielectric function and the  $f$ -sum rule. In Sec. III a method for analyzing optical experiments is presented and its application to the analysis of data from Si is demonstrated and discussed.

### II. MODEL DIELECTRIC FUNCTION

#### A. Construction of $\epsilon_2(\omega)$

The formal expression for the complex dielectric function within the RPA involves sums over wave vectors and over all the energy bands between which transitions occur.<sup>2d,12</sup> The explicit calculation of the dielectric function requires knowledge of the band structure of the material, evaluated according to some model. In our formulation we divide the energy spectrum of the material into two parts. The first part is described via a two-band scheme and accounts for contributions to the dielectric function from electronic transitions connecting the valence band and the conduction band up to a certain energy (to be specified below). The second part of the spectrum which accounts for transitions to high-lying energy states is incorporated into the model via an approximation to

the RPA dielectric function.

An expression for the dielectric function  $\epsilon(\omega)$ , based on a simple two-band Hamiltonian, has been recently proposed by Chadi and White.<sup>6</sup> They employed a Hamiltonian which in the tight-binding (Wannier) representation (a natural choice for covalently bonded materials) is given as

$$H = V_0 \sum_{i \neq i'} |v, i\rangle \langle v, i'| + (V_0 + V_1) \sum_{i \neq i'} |c, i\rangle \langle c, i'| + E_g \sum_i |c, i\rangle \langle c, i|, \quad (1)$$

where  $c$  ( $v$ ) designates the conduction (valence) band,  $i$  is an atomic site index, and only nearest-neighbor interactions are included. The band structure corresponding to the above Hamiltonian for a  $z$ -fold atomically coordinated system ( $z = 4$  for Si), is characterized by a valence band and a conduction band of widths  $|2zV_0|$  and  $|2z(V_0 + V_1)|$ , respectively, and an average gap  $E_g$ . In the derivation an integral form of the RPA dielectric function written in the tight-binding representation has been used with the dipole approximation, and the site approximation, which states that the only nonzero matrix elements of  $x$  are between two sites on the same orbital, i.e.,

$$|\langle v, i | x | c, j \rangle|^2 = |x_{vc}|^2 \delta_{ij}. \quad (2)$$

In order to achieve a closed form expression, a Bethe lattice topology<sup>6,13</sup> has been used yielding the following expression for  $\epsilon_2$  (for four-fold coordination):

$$\epsilon_2^{\text{CW}}(\omega) = \alpha [12V_1^2 - (\hbar\omega - E_g)^2]^{1/2} [16V_1^2 - (\hbar\omega - E_g)^2]^{-1}, \quad (3)$$

for  $E_g - \sqrt{12}V_1 \leq \hbar\omega \leq E_g + \sqrt{12}V_1$ , and  $\epsilon_2^{\text{CW}}(\omega) = 0$  otherwise. In the above  $\alpha = 8\pi n e^2 |x_{vc}|^2$ ,  $n$  is the electron density and  $x_{vc}$  is determined by the site approximation of the dipole matrix element [see Eq. (2)].

$\epsilon_2^{\text{CW}}$ , given in Eq. (2), exhibits a two-peak structure characteristic to elemental and III-V semiconductors (for example, 2.3 and 4.4 eV in<sup>4a</sup> Ge; 3.4 and 4.3 eV in<sup>4b</sup> Si; the split spin orbit peaks at 2.88, 3.15, and 5.0 eV in<sup>14</sup> GaAs). In Fig. 1 we show the imaginary part of the dielectric function,  $\epsilon_2^{\text{CW}}$  as given by Eq. (3) with parameters appropriate for Si (see Sec. III.) Although the above prominent features are obtained from the above dielectric function, it is important to recognize that by construction, only transitions in the range  $0 \leq \hbar\omega \leq E_g + \sqrt{12}V_1$  have been considered. Moreover, for typical values of the model parameters  $\alpha$ ,  $E_g$ , and  $V_1$  (which are determined as described in Sec. III), only about 50% of the  $f$ -sum rule<sup>1</sup>

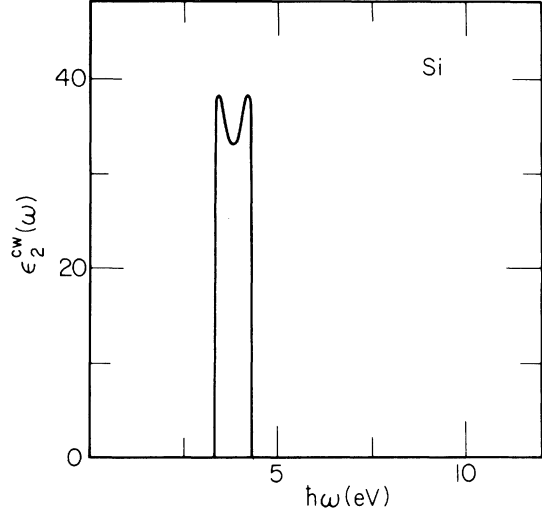


FIG. 1. Imaginary part of the dielectric function,  $\epsilon_2^{\text{CW}}(\omega)$  [see Eq. (3)] with parameters appropriate for Si:  $E_g = 3.80$ ,  $V_1 = 0.16$  eV (see discussion in Sec. III of the text).

$$\int_0^\infty \omega \epsilon_2(\omega) d\omega = (\frac{1}{2}\pi) \omega_p^2 \quad (4)$$

is exhausted by  $\epsilon_2^{\text{CW}}$  ( $\hbar\omega_p = 16.6$  eV for Si).

The optical constants for higher frequencies do not exhibit sharp structure.<sup>2d</sup> For semiconductors which have a single group of valence bands (like Si, SiC, AlP) that is energetically isolated from the core states ( $\sim 80$  eV for Si), asymptotic expressions (of the Drude or Drude-like type) for the RPA dielectric function were obtained by Philipp and Ehrenreich.<sup>15</sup> The derivation of the asymptotic formulas by these authors is based on the explicit expression for the complex dielectric function of an insulator in the random phase approximation which is given as<sup>2d</sup>

$$\epsilon(\omega) = 1 - \frac{e^2}{\pi^2 m} \int d^3k \sum_{ll'} f_{l\vec{k}} f_{l'\vec{k}}^\mu B_{ll'} \times \left( \omega + \omega_{ll'} + i \frac{\Gamma_{ll'}}{2} \right)^{-1} \times \left( \omega - \omega_{ll'} + i \frac{\Gamma_{ll'}}{2} \right)^{-1}, \quad (5)$$

and the use of the  $f$ -sum rule

$$\int d^3k \sum_{ll'} f_{l\vec{k}} f_{l'\vec{k}}^\mu = 4\pi^3 n. \quad (6)$$

In the above,  $l$  is a band index,  $f_{l\vec{k}}$  is the free Fermi distribution function (either 1 or 0),  $f_{l'\vec{k}}^\mu$  is the  $\mu$ th component of the oscillator strength of transitions between  $l$  and  $l'$ ,  $n$  is the electrons number density,  $\frac{1}{2}\Gamma_{ll'}$  is the damping parameter,

related to the relaxation time  $\tau_{11'}$ , ( $\frac{1}{2}\Gamma_{11'} \equiv 1/\tau_{11'}$ ), and the transition frequency  $\omega_{11'}$  is given by

$$\hbar\omega_{11'} = E_{1'}(k) - E_1(k). \quad (7)$$

The term  $B_{11'}$  in Eq. (5) depends on the model taken for the collisional damping of the electrons.<sup>2a,16</sup> For high frequencies  $\omega \gg \omega_{11'}$ , and assuming the same damping parameter for all valence bands ( $\Gamma_{1v} \equiv \Gamma$ ), the following results are obtained.<sup>2d</sup>

(a) For  $B_{11'} = 1$ , a "Drude-like" expression<sup>17</sup> is obtained

$$\epsilon(\omega) = 1 - \omega_p^2 / (\omega + \frac{1}{2}i\Gamma)^2, \quad (8)$$

where  $\omega_p = 4\pi e^2 \sum_v n_v / m$  is the free-electron plasma frequency of the valence bands ( $n_v$  is the valence electron density). From Eq. (8),

$$\epsilon_2(\omega) = \omega_p^2 \Gamma \omega / (\omega^2 + \frac{1}{4}\Gamma^2)^2. \quad (9)$$

(b) For  $B_{11'} = 1 + i\Gamma/2\omega$ , the Drude formula is obtained

$$\epsilon(\omega) = 1 - \omega_p^2 / \omega(\omega + \frac{1}{2}i\Gamma). \quad (10)$$

These formulas show that for large frequencies the valence electrons behave as free particles. Since the frequency range in which we are interested (above the highest frequency of the "two-band" portion of the spectrum,  $\hbar\omega \geq E_g + \sqrt{12}V_1$ ) may start at a value which is lower than the one for which the asymptotic formulas [Eqs. (8) and (10)] were originally derived, we modify the derivation as follows: the electrons are regarded as classical Lorentz oscillators tied to the lattice sites with frequencies  $\omega_{11'}$ . Since we are dealing with transitions from the valence band to high-lying states in the conduction bands, we replace  $\omega_{11'}$  in Eq. (5) by a characteristic "mean" frequency  $\omega_0$ . This approximation yields the following results.

(c)  $B_{11'} = 1$ , the Lorentz-like expressions are obtained

$$\epsilon^I(\omega) = 1 - \omega_p^2 / [\omega^2 - (\omega_0^2 + \frac{1}{4}\Gamma^2) + i\Gamma\omega] \quad (11)$$

and

$$\epsilon_2^I(\omega) = \omega_p^2 \Gamma \omega / \{[\omega^2 - (\omega_0^2 + \frac{1}{4}\Gamma^2)]^2 + \Gamma^2 \omega^2\}, \quad (12)$$

which reduce to the corresponding Drude-like expressions [Eqs. (8) and (9)] when  $\omega_0 = 0$ .

Having obtained the expressions for the imaginary part of the dielectric function in the two frequency ranges [Eqs. (3) and (12)] we wish to combine them into an  $\epsilon_2$  function for all frequencies ( $\omega \geq 0$ ).

In constructing the combined function, the two parts,  $\epsilon_2^{\text{CW}}$  and  $\epsilon_2^I$ , have to be matched such, that

the resulting function will be continuous both in value and slope at the matching region. This is of particular importance since discontinuities in  $\epsilon_2(\omega)$  cause logarithmic singularities in the real part of<sup>18</sup>  $\epsilon_1(\omega)$  which is derived from  $\epsilon_2$  via the Kramers-Kronig relation (see Sec. II B). Thus, we introduce a function  $L(\omega)$  defined as

$$L(\omega) = 1 + C[\hbar(\omega - \omega_a) + D]^{-1}, \quad (13)$$

where  $\hbar\omega_a = E_g + \sqrt{12}V_1 - \Delta$ , with  $\Delta$  a cutoff parameter whose determination is discussed in Sec. III (typically,  $\Delta \sim 0.05$  eV), and  $C$  and  $D$  are constants to be described below. The modified expression for  $\epsilon_2$  in the range  $\omega \geq \omega_a$  is written

$$\epsilon_2^{LI}(\omega) = L(\omega)\epsilon_2^I(\omega), \quad (14)$$

where  $\epsilon_2^I$  is given by Eq. (12). It is noted that since  $L(\omega)$  tends to unity as  $\omega > \omega_a$ , the modified function  $\epsilon_2^{LI} \rightarrow \epsilon_2^I$  for these frequencies. The imaginary part of the dielectric function for all frequencies ( $\omega \geq 0$ ) can now be written

$$\epsilon_2(\omega) = \Theta(\omega_a - \omega)\epsilon_2^{\text{CW}}(\omega) + \Theta(\omega - \omega_a)\epsilon_2^{LI}(\omega), \quad (15)$$

where  $\Theta(x)$  is the step function (which is equal to 1,  $\frac{1}{2}$ , or 0 for  $x > 0$ ,  $x = 0$ , or  $x < 0$ , respectively). The constants  $C$  and  $D$  in the function  $L$  [Eq. (13)] are determined by demanding continuity of value and slope of  $\epsilon_2$  [Eq. (15)] at  $\omega_a$ , yielding

$$D = A\epsilon_2^I(\omega_a)[(A+1)\epsilon_2^{II}(\omega_a) - \epsilon_2^{\text{CW}}(\omega_a)]^{-1}, \quad (16a)$$

$$C = AD, \quad A = [\epsilon_2^{\text{CW}}(\omega_a)/\epsilon_2^I(\omega_a)] - 1, \quad (16b)$$

where  $\epsilon_2^I(\omega_a)$  denotes the derivative evaluated at  $\omega_a$ .

#### B. Construction of $\epsilon_1(\omega)$ via the Kramers-Kronig relation

The real and imaginary parts of a causal dielectric function are related to each other by the Kramers-Kronig relations,<sup>1</sup> given as

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (17)$$

where P designates that the integral is to be evaluated in the principal value sense. In this context we remark that discontinuities in value and/or slope in  $\epsilon_2$  result in logarithmic singularities in the integration in Eq. (17). The continuity of  $\epsilon_2(\omega)$  [Eq. (15)] achieved via the function  $L(\omega)$  [Eq. (13)] avoids this problem. Substituting in Eq. (17), the expression for the imaginary part  $\epsilon_2$  given in Eq. (15), and using the definition of the function  $L(\omega)$ , the following expression is obtained:

$$\begin{aligned}
\epsilon_1(\omega) - 1 &= \frac{2}{\pi} \left( P \int_0^{\omega_a} \frac{\omega' \epsilon_2^{CW}(\omega')}{\omega'^2 - \omega^2} d\omega' \right. \\
&\quad + P \int_{\omega_a}^{\infty} \frac{\omega' \epsilon_2^I(\omega')}{\omega'^2 - \omega^2} d\omega' \\
&\quad \left. + C P \int_{\omega_a}^{\infty} \frac{\omega' \epsilon_2^I(\omega')}{(\omega' - \eta)(\omega'^2 - \omega^2)} d\omega' \right) \\
&\equiv I_1 + I_2 + C J_3, \tag{18}
\end{aligned}$$

where  $\eta = (\hbar\omega_a - D)/\hbar$  [see Eq. (13)]. The evaluation of the integrals in Eq. (18) is given in Appendix A.

### C. Evaluation of the $f$ -sum rule

The  $f$ -sum rule [Eq. (4)], relates the imaginary part of the dielectric function and the plasma frequency  $\omega_p$ . An analytical expression for the sum rule, which enables its evaluation and an examination of the dependence on the model parameters can be derived by substituting  $\epsilon_2(\omega)$  given by Eq. (15) in Eq. (4). Using the definition of  $\epsilon_2^{CW}$  given in Eq. (3), the following expression is obtained:

$$\alpha J_1 + J_2 = \left(\frac{1}{2}\pi\right) \omega_p^2, \tag{19}$$

where

$$\begin{aligned}
J_1 &= \int_{(E_g - G)/\hbar}^{(E_g + G - \Delta)/\hbar} \omega [G^2 - (\hbar\omega - E_g)^2]^{1/2} \\
&\quad \times [16V_1^2 - (\hbar\omega - E_g)^2]^{-1} d\omega, \tag{20a}
\end{aligned}$$

$$J_2 = \int_{(E_g + G - \Delta)/\hbar}^{\infty} \omega L(\omega) \epsilon_2^I(\omega) d\omega, \tag{20b}$$

where, as before,  $G = 2\sqrt{3} V_1$ ,  $L(\omega)$  is defined in Eq. (13), and  $\epsilon_2^I(\omega)$  is given in Eq. (12). Explicit expressions for the integrals  $J_1$  and  $J_2$  are given in Appendix B.

### III. DETERMINATION OF MODEL PARAMETERS: Si

The model dielectric function constructed in Sec. II contains the following parameters: the average gap energy  $E_g$ , the width parameter  $V_1$ , the scale parameter  $\alpha$  [Eq. (3)], the damping parameter  $\Gamma$  [Eq. (12)], the frequency  $\omega_0$  [Eq. (12)], and the cutoff  $\Delta$  [and thus  $\omega_a$ , Eq. (13)]. On first sight this seems to be a multitude of parameters which would hinder meaningful quantitative analysis. However, a closer examination reveals that this is not the case, due to the fact that the parameters determine distinct (and different) features of the spectra and all but the last one have clear physical significance. The values of the parameters are determined by inspection of the data and a consistent variation of  $\Gamma$ ,  $\Delta$ , and  $\omega_0$  dictated by the  $f$ -sum rule. Clearly, the values of the parameters depend on the extent of data used. Our analysis

employs optical data over the entire frequency range of measurement, hence the resulting values are expected to be more accurate than those obtained on the basis of a limited range.

The value of the parameter  $V_1$  is obtained by fitting the width of  $\epsilon_2$  in the vicinity of the local minimum between the two peaks mentioned previously. This determines the positions of the maxima in  $\epsilon_2$  and the average gap  $E_g$ , which is taken at midwidth. The scaling parameter  $\alpha$ , which is related to the strength of the dipole matrix element [Eqs. (2) and (3)], is determined by aligning the height of the maximum in the model  $\epsilon_2$  with the average height of the experimental maxima. An initial value for the damping  $\Gamma$  is obtained by fitting the model and experimental  $\epsilon_2$  in the frequency range  $\hbar\omega \geq 7.5$  eV (approximately, frequency region 2 in the notation of Ref. 2d). Subsequently, initial values for the cutoff  $\Delta$  and the "Lorentz frequency"  $\omega_0$  are determined through fitting in the region  $\hbar\omega \geq E_g + \sqrt{12}V_1 - \Delta$ . Finally, the  $f$ -sum rule is evaluated and a variation of  $\Gamma$  and  $\omega_0$  is performed to satisfy the sum rule [right-hand side of Eq. (4)]. Using the analytical formula for  $\epsilon_1(\omega)$  derived from the Kramers-Kronig relation, with the above parameters, the complex dielectric function [ $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ ] is obtained.

In the following, we apply our model to the analysis of optical properties of Si. Using the data of Philipp and Ehrenreich,<sup>2d</sup> we obtain the imaginary and real part of the dielectric function shown in Figs. 2 and 3, respectively (dotted curves). For comparison we include in the figures the results of some previous studies. The degrees of

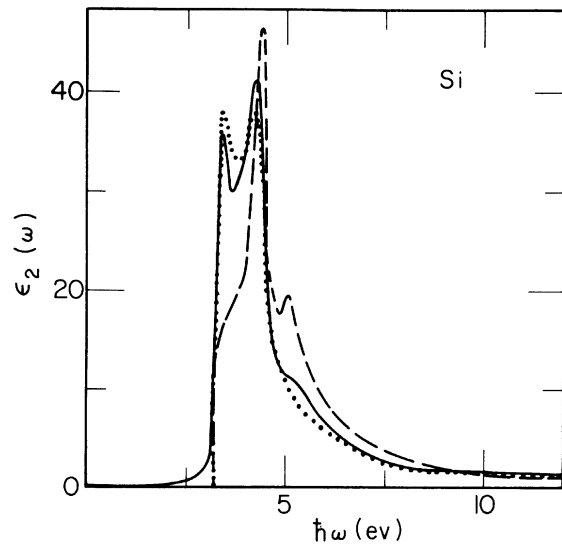


FIG. 2.  $\epsilon_2(\omega)$  for Si. Experimental data after Ref. 2(d) (solid line), present calculation (dots), and empirical pseudopotential results after Ref. 19 (dashed line).

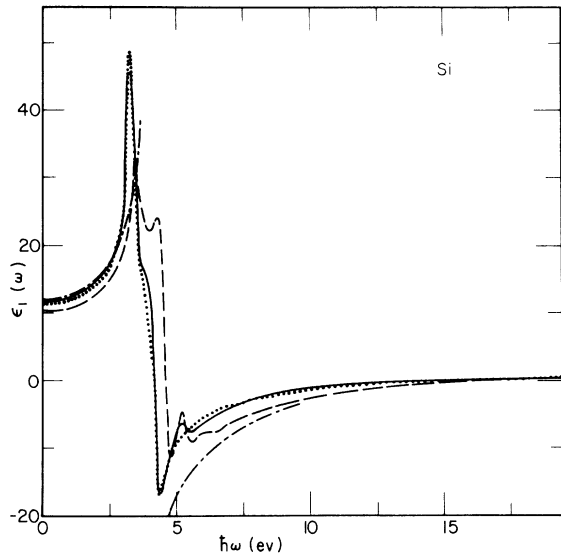


FIG. 3.  $\epsilon_1(\omega)$  for Si obtained from  $\epsilon_2(\omega)$  via analytical Kramers-Kronig relation. Data, Ref. 2(d) (solid). Present calculation (dots), nearly-free-electron model (after Ref. 10, dash-dotted line), and empirical pseudopotential calculation (after Ref. 19, dashed line).

agreement achieved in the present study clearly exceed those of other calculations. Values of the best-fit parameters used in the calculation were  $E_g = 3.80$ ,  $V_1 = 0.16$ ,  $\hbar\Gamma = 4.86$ , and  $\Delta = 0.04$  eV and  $\omega_0 = 0.0$ . The sum rule was *satisfied exactly* and the value of the resulting static dielectric function  $\epsilon_1(0)$  is 11.0, in good agreement with experiment. It is of interest to note that the value of the "mean" frequency in the "Lorentz-like" expression for the dielectric function [Eqs. (11) and (12)], which was determined by best fitting to the data, is zero, indicating that for excitation frequencies in the range  $\hbar\omega \geq E_g + \sqrt{12}V_1$  the valence electrons of Si behave as "freelike" particles. We also remark on the rapid approach of the function  $L(\omega)$  [Eq. (13)] to unity as illustrated in Fig. 4. This demonstrates that the operation of this function is limited to the matching region (the purpose for which it was introduced).

In conclusion, it is instructive to compare our

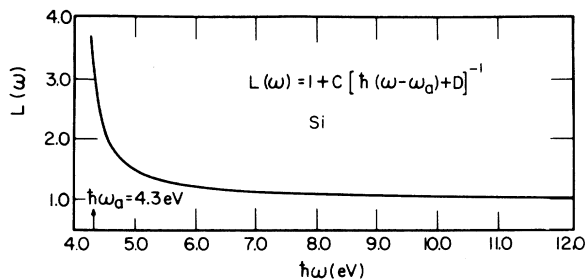


FIG. 4. Matching function  $L(\omega)$  [see Eqs. (13) and (16)] for Si. Note the rapid approach to unity.

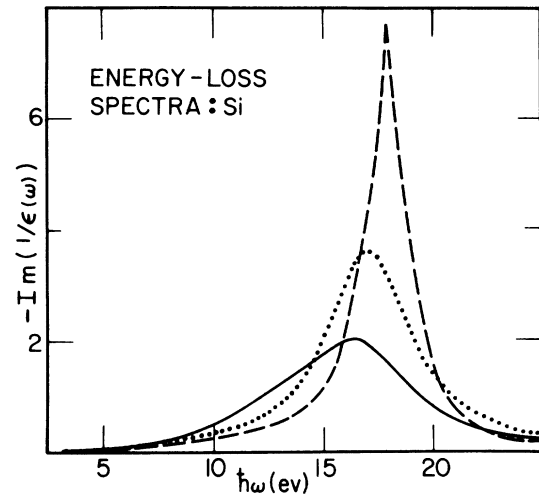


FIG. 5. Energy-loss spectrum for Si. Data after Ref. 2(d) (solid line), present calculation (dots), and empirical pseudopotential with no local-field corrections (Ref. 19, dashed line).

results with some previous studies. In a recent calculation<sup>10</sup> using an isotropic nearly-free-electron band approximation, the sum rule was obeyed to only  $\sim 83\%$ , a value of  $E_g = 3.92$  eV was found, and the quantitative agreement with experiment was rather limited. Most recently, in calculations based on the empirical pseudopotential method,<sup>19</sup> an approximate satisfaction of the sum rule was achieved and a value of 10.1 (compared to the experimental value<sup>2d</sup> of  $\sim 11.8$ ) for  $\epsilon_1(0)$  was obtained<sup>20</sup> (see dashed curve in Fig. 3). Furthermore, a high value for  $E_g$  (5.36 eV) was obtained by Chadi and White.<sup>6</sup> This originates from their analysis of a restricted range of low-frequency (0.1–1.2-eV) data.

Finally, we have used our results for the complex dielectric function in calculations of the reflectivity and the energy-loss spectrum  $\{-\text{Im}[1/\epsilon(\omega)]\}$  of Si, obtaining good agreement with experiment. For illustration we show in Fig. 5 the loss spectra for Si (dotted line) obtained from the dielectric functions shown in Figs. 2 and 3, and compare it with the observed spectra (solid line) and with the results of a recent study.<sup>19</sup> We are currently using the method for the analysis of data from other semiconductors and will report our results in due course.

#### ACKNOWLEDGMENTS

We would like to thank Professor E. W. Montröll and Professor E. Wolf for their interest and helpful remarks. We thank Professor M. L. Cohen for supplying us with the results of the real part of the dielectric function which are included in Fig. 3.

## APPENDIX A

In this appendix we evaluate the integrals appearing in the Kramers-Kronig expression for  $\epsilon_1(\omega)$  [Eq. (18)].

(i) The integral  $I_1$  in Eq. (18) is given by

$$I_1 = \frac{2}{\pi} \text{P} \int_0^{\omega_a} \frac{\omega' \epsilon_2^{\text{CW}}(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (\text{A1})$$

Substituting for  $\epsilon_2^{\text{CW}}$  the expression given by Eq. (3) and expanding the denominator in partial fractions, the integral can be written

$$I_1 = \alpha(I_1^- + I_1^+), \quad (\text{A2})$$

$$I_1^- = \pi^{-1} \int_{-G}^{G-\Delta} (G^2 - x^2)^{1/2} \times [(16V_1^2 - x^2)(x - y)]^{-1} dx, \quad (\text{A3a})$$

$$I_1^+ = \pi^{-1} \int_{-G}^{G-\Delta} (G^2 - x^2)^{1/2} \times [(16V_1^2 - x^2)(x + y + 2E_g)]^{-1} dx, \quad (\text{A3b})$$

where  $G = 2\sqrt{3}V_1$  and  $y = \hbar\omega - E_g$ . Expanding the denominators in Eqs. (A3a) and (A3b) in partial fractions we obtain

$$I_1^- = a_- I_{1a}^- + b_- I_{1b}^- + c_- I_{1c}^-, \quad (\text{A4a})$$

$$I_1^+ = a_+ I_{1a}^+ + b_+ I_{1b}^+ + c_+ I_{1c}^+, \quad (\text{A4b})$$

with the coefficients

$$a_- = (16V_1^2 - y^2)^{-1}, \quad (\text{A5a})$$

$$b_- = [8V_1(4V_1 - y)]^{-1}, \quad (\text{A5b})$$

$$c_- = -[8V_1(4V_1 + y)]^{-1} \quad (\text{A5c})$$

and

$$a_+ = [16V_1^2 - (y + 2E_g)^2]^{-1}, \quad (\text{A6a})$$

$$b_+ = [8V_1(y + 2E_g + 4V_1)]^{-1}, \quad (\text{A6b})$$

$$c_+ = [8V_1(y + 2E_g - 4V_1)]^{-1}. \quad (\text{A6c})$$

The integrals  $I_{a,b,c}^\pm$  are evaluated in Appendix C.

(ii) The integral  $I_2$  in Eq. (18) is given by

$$I_2 = \frac{2}{\pi} \text{P} \int_{\omega_a}^{\infty} \frac{\omega' \epsilon_2^I(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (\text{A7})$$

where  $\epsilon_2^I$  is given by Eq. (12). The above integral can be written

$$I_2 = \epsilon_1^I(\omega) - 1 - J(\omega), \quad (\text{A8a})$$

$$\epsilon_1^I(\omega) = 1 - \frac{\omega_p^2[\omega^2 - (\omega_0^2 + \frac{1}{4}\Gamma^2)]}{[\omega^2 - (\omega_0^2 + \frac{1}{4}\Gamma^2)]^2 + \Gamma^2\omega^2}, \quad (\text{A8b})$$

and

$$J(\omega) = \pi^{-1} \int_{-\omega_a}^{\omega_a} \frac{\epsilon_2^I(\omega')}{\omega' - \omega} d\omega'. \quad (\text{A8c})$$

It can be shown that the integral  $J(\omega)$  in the above equation is equal to

$$J(\omega) = \epsilon_1^I(\omega) \ln \left| \frac{\omega_a - \omega}{\omega_a + \omega} \right| + \pi^{-1}(\beta_1 - \gamma_1) \ln \left( \frac{(\omega_a - \Omega_1)^2 + \Omega_2^2}{(\omega_a + \Omega_1)^2 + \Omega_2^2} \right) + 2\pi^{-1}(\gamma_2 - \beta_2) \left[ \tan^{-1} \left( \frac{\omega_a + \Omega_1}{\Omega_2} \right) + \tan^{-1} \left( \frac{\omega_a - \Omega_1}{\Omega_2} \right) \right], \quad (\text{A9})$$

where

$$\Omega \equiv \Omega_1 + i\Omega_2 = \omega_0 + \frac{1}{2}i\Gamma, \quad (\text{A10a})$$

$$\beta_1 + i\beta_2 = i\omega_p^2/[4\omega_0(\omega - \Omega)], \quad (\text{A10b})$$

$$\gamma_1 + i\gamma_2 = i\omega_p^2/[4\omega_0(\omega + \Omega)]. \quad (\text{A10c})$$

(iii) The integral  $I_3$  is given by

$$I_3 = \frac{2}{\pi} \text{P} \int_{\omega_a}^{\infty} \frac{\omega' \epsilon_2^I(\omega')}{(\omega' - \eta)(\omega'^2 - \omega^2)} d\omega', \quad (\text{A11})$$

where  $\eta = (\hbar\omega_a - D)/\hbar$ . Using a partial fraction expansion, a direct integration yields

$$I_3 = \pi^{-1} \left\{ a_3 \ln(D/\hbar) + b_3 \ln|\omega_a - \omega| + b'_3 \ln(\omega_a + \omega) - (c_{3,r} + c'_{3,r}) \ln[(\omega_a - \Omega_1)^2 + \Omega_2^2] + 2(c_{3,i} + c'_{3,i}) \left[ \tan^{-1} \left( \frac{\omega_a - \Omega_1}{\Omega_2} \right) - \frac{\pi}{2} \right] - (d_{3,r} + d'_{3,r}) \ln[(\omega_a + \Omega_1)^2 + \Omega_2^2] - 2(d_{3,i} + d'_{3,i}) \left[ \tan^{-1} \left( \frac{\omega_a + \Omega_1}{\Omega_2} \right) - \frac{\pi}{2} \right] \right\}, \quad (\text{A12})$$

where

$$a_3 = 2\eta\epsilon_2^I(\eta)/(\omega^2 - \eta^2), \quad (\text{A13a})$$

$$b_3 = \epsilon_2^I(\eta)/(\eta - \omega), \quad (\text{A13b})$$

$$b'_3 = -\epsilon_2^I(\eta)/(\eta + \omega), \quad (\text{A13c})$$

$$c_{3,r} + ic_{3,i} = -i(\omega_p^2/4\omega_0)[(\Omega - \eta)(\Omega - \omega)]^{-1}, \quad (\text{A13d})$$

$$c'_{3,r} + ic'_{3,i} = -i(\omega_p^2/4\omega_0)[(\Omega - \eta)(\Omega + \omega)]^{-1}, \quad (\text{A13e})$$

$$d_{3,r} + id_{3,i} = -i(\omega_p^2/4\omega_0)[(\Omega + \eta)(\Omega + \omega)]^{-1}, \quad (\text{A13f})$$

$$d'_{3,r} + id'_{3,i} = -i(\omega_p^2/4\omega_0)[(\Omega + \eta)(\Omega - \omega)]^{-1} \quad (\text{A13g})$$

and  $\Omega$  is defined in Eq. (A10a).

## APPENDIX B

In this appendix we evaluate the integrals which occur in the expression for the  $f$ -sum rule [Eqs. (19), (20a), and (20b)]. The integral  $J_1$  [Eq. (20a)] can be decomposed in the following way:

$$\hbar^2 J_1 = J_1^+(E_g/4V_1 - 1) + J_1^-(E_g/4V_1 + 1), \quad (\text{B1})$$

where

$$J_1^+ = \frac{1}{2} \int_{-G}^{G-\Delta} (G^2 - x^2)^{1/2} (4V_1 + x)^{-1} dx, \quad (\text{B2a})$$

$$J_1^- = \frac{1}{2} \int_{-G}^{G-\Delta} (G^2 - x^2)^{1/2} (4V_1 - x)^{-1} dx. \quad (\text{B2b})$$

These integrals can be evaluated with the help of the formulas in Appendix C yielding

$$J_1^+ = (\frac{1}{2}\pi) I_{1c}^-, \quad (\text{B3a})$$

where  $I_{1c}^-$  is given by Eq. (C5c), and

$$J_1^- = (\pi/2) I_{1b}^-, \quad (\text{B3b})$$

and  $I_{1b}^-$  given by Eq. (C5b). Using the definition of the function  $L(\omega)$  given in Eq. (13), the integral  $J_2$  [Eq. (20b)] is written

$$J_2 = \int_{\omega_a}^{\infty} \omega \epsilon_2^+(\omega) d\omega + C \int_{\omega_a}^{\infty} \frac{\omega \epsilon_2^+(\omega)}{\omega - \eta} d\omega \\ \equiv J_{2,1} + C J_{2,2}, \quad (\text{B4})$$

where  $\eta = (\hbar \omega_a - D)/\hbar$ . Using the sum rule for the Lorentzian dielectric function,  $J_{2,1}$  can be written

$$J_{2,1} = (\frac{1}{2}\pi) \omega_p^2 - \omega_p^2 \Gamma K_1, \quad (\text{B5})$$

and  $K_1$  is given by

$$K_1 = \delta_1 \ln \left( \frac{(\omega_a - \Omega_1)^2 + \Omega_2^2}{(\omega_a + \Omega_1)^2 + \Omega_2^2} \right) \\ - 2\delta_2 \left[ \tan^{-1} \left( \frac{\omega_a + \Omega_1}{\Omega_2} \right) + \tan^{-1} \left( \frac{\omega_a - \Omega_1}{\Omega_2} \right) \right], \quad (\text{B6a})$$

$\Omega_1$  and  $\Omega_2$  are given by Eq. (A10a), and

$$\delta_1 + i\delta_2 = 1/8\omega_0 - i/4\Gamma. \quad (\text{B6b})$$

The integral  $J_{2,2}$  is given by

$$J_{2,2} = \omega_p^2 \Gamma \left[ -\alpha \ln(\omega_a - \eta) - \lambda_1 \ln[(\omega_a - \Omega_1)^2 + \Omega_2^2] \right. \\ \left. - \mu_1 \ln[(\omega_a + \Omega_1)^2 + \Omega_2^2] \right. \\ \left. + 2\lambda_2 \tan^{-1} \left( \frac{\omega_a - \Omega_1}{\Omega_2} \right) \right. \\ \left. - 2\mu_2 \tan^{-1} \left( \frac{\omega_a + \Omega_1}{\Omega_2} \right) + \pi(\mu_2 - \lambda_2) \right], \quad (\text{B7})$$

where  $\Omega_1$  and  $\Omega_2$  are given in Eq. (A10a) and

$$\alpha = \eta^2 / [(\eta^2 - \Omega_1^2)(\eta^2 - \Omega_2^2)], \quad (\text{B8a})$$

$$\lambda_1 + i\lambda_2 = i\Omega_1/8\Omega_1\Omega_2(\eta - \Omega_1), \quad (\text{B8b})$$

$$\mu_1 + i\mu_2 = -i\Omega_2/8\Omega_1\Omega_2(\eta + \Omega_1). \quad (\text{B8c})$$

### APPENDIX C

In this appendix we evaluate the Hilbert transform of a function  $f(x)$ , defined as

$$f(x) = \begin{cases} (G^2 - x^2)^{1/2} & \text{for } -G \leq x \leq G - \Delta, \\ 0 & \text{otherwise,} \end{cases} \quad (\text{C1})$$

and  $G > \Delta > 0$ . The Hilbert transform of this function is given by

$$F(y) = \pi^{-1} \text{P} \int_{-\infty}^{\infty} \frac{f(x)}{x - y} dx \\ = \pi^{-1} \text{P} \int_{-G}^{G-\Delta} \frac{(G^2 - x^2)^{1/2}}{x - y} dx. \quad (\text{C2})$$

In evaluating the above integral, we distinguish several cases depending on the value of the variable  $y$ . Using the following definitions,

$$\delta = G - \Delta, \quad (\text{C3a})$$

$$Q(z) = (G^2 - z^2)^{1/2}, \quad (\text{C3b})$$

$$R = \frac{1}{2}\pi + \sin^{-1}(\delta/G), \quad (\text{C3c})$$

$$S(z) = \frac{1}{2}\pi + \sin^{-1} \left( \frac{G^2 - \delta z}{G(\delta - z)} \right), \quad (\text{C3d})$$

$$T_{\pm}(z) = [Q(z)Q(\delta) + G^2 - \delta z] / [\pm G(\delta - z)]; \quad (\text{C3e})$$

the integral  $F(y)$  [Eq. (C2)] is given by

$$y \leq -G, \quad F_1(y) = \pi^{-1} [Q(\delta) - Ry - S(y)(y^2 - G^2)^{1/2}]; \quad (\text{C4a})$$

$$-G \leq y \leq G - \Delta, \quad F_2(y) = \pi^{-1} [Q(\delta) - Ry - Q(y) \ln T_+(y)]; \quad (\text{C4b})$$

$$\delta \leq y \leq G, \quad F_3(y) = \pi^{-1} [Q(\delta) - Ry - Q(y) \ln T_-(y)]; \quad (\text{C4c})$$

$$y \geq G, \quad F_4(y) = \pi^{-1} [Q(\delta) - Ry + S(y)(y^2 - G^2)^{1/2}]. \quad (\text{C4d})$$

Using these results the integrals in Eqs. (A4a) and (A4b) can be written

$$I_{1a}^- = F_j \quad (j = 1, 2, 3, 4 \text{ for the} \\ \text{corresponding values of } y). \quad (\text{C5a})$$

$$I_{1b}^- = -F_4(4V_1), \quad (\text{C5b})$$

$$I_{1c}^- = F_1(-4V_1), \quad (\text{C5c})$$

$$I_{1a}^+ = F_1[-(y + 2E_g)], \quad (\text{C5d})$$

$$I_{1b}^+ = I_{1b}^- \text{ and } I_{1c}^+ = I_{1c}^-. \quad (\text{C5e})$$

- <sup>†</sup>Research partially supported by the Army Research Office and the General Electric Foundation.
- <sup>\*</sup>Institute for Fundamental Studies and Department of Physics and Astronomy.
- <sup>1</sup>(a) F. Bassani and G. P. Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, 1975); (b) F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).
- <sup>2</sup>(a) F. Stern, *Solid State Phys.* 15, 300 (1963); (b) J. C. Phillips, *ibid.* 18, 55 (1966); (c) M. L. Cohen and V. Heine, *ibid.* 24, 38 (1970); (d) H. R. Philipp and H. Ehrenreich, *Semicond. Semimet.* 3, 93 (1967).
- <sup>3</sup>H. Ehrenreich, H. R. Philipp, and J. C. Phillips, *Phys. Rev. Lett.* 8, 59 (1962).
- <sup>4</sup>(a) D. Brust, J. C. Phillips, and F. Bassani, *Phys. Rev. Lett.* 9, 94 (1962); (b) D. Brust, M. L. Cohen, and J. C. Phillips, *ibid.* 9, 389 (1962).
- <sup>5</sup>D. R. Penn, *Phys. Rev.* 128, 2093 (1962).
- <sup>6</sup>D. J. Chadi and R. M. White, *Phys. Rev. B* 11, 5077 (1975), and references therein.
- <sup>7</sup>J. C. Phillips, *Rev. Mod. Phys.* 42, 317 (1970); J. A. Van Vechten, *Phys. Rev.* 182, 891 (1969).
- <sup>8</sup>J. Callaway, *Phys. Rev.* 116, 1638 (1958).
- <sup>9</sup>E. Tosatti and G. P. Parravicini, *J. Phys. Chem. Solids* 32, 623 (1971). In this study a consistent analysis of the free-electron model dielectric function was performed. The derived expressions satisfy the Kramers-Kronig relation and the  $f$ -sum rule by construction.
- <sup>10</sup>R. A. Breckenridge, R. W. Shaw, Jr., and A. Sher, *Phys. Rev. B* 10, 2483 (1974).
- <sup>11</sup>A. Bardasis and D. Hone, *Phys. Rev.* 153, 849 (1967).
- <sup>12</sup>H. Ehrenreich and M. H. Cohen, *Phys. Rev.* 115, 786 (1959).
- <sup>13</sup>M. F. Thorpe and D. Weaire, *Phys. Rev. B* 10, 3518 (1971).
- <sup>14</sup>J. P. Walter and M. L. Cohen, *Phys. Rev.* 183, 763 (1969).
- <sup>15</sup>See Ref. 2(d). Similar, but more complicated expressions were derived by these authors for the case of two separated groups of filled bands.
- <sup>16</sup>H. Ehrenreich and H. R. Philipp, *Phys. Rev.* 128, 1622 (1962), in particular, Sec. III.
- <sup>17</sup>See Ref. 2(d), Eq. 23. A similar expression was used in Ref. 14 for the analytical tail of  $\epsilon_2$ .
- <sup>18</sup>H. Bode, *Network Analysis and Feedback Amplifier Design* (Van Nostrand, New York, 1945).
- <sup>19</sup>S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, *Phys. Rev. Lett.* 34, 155 (1975).
- <sup>20</sup>This  $\epsilon_1(\omega)$  is related via the Kramers-Kronig relation to the corresponding  $\epsilon_2(\omega)$  which was given in Ref. 19, and is shown as the dashed curve in our Fig. 2. The  $\epsilon_1(\omega)$  curve which was not shown in the original publication (Ref. 19) was kindly supplied to us by Professor M. L. Cohen.