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Optical properties of crystalline semiconductors and dielectrics

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A new formulation for the complex index of refraction, $N(E)=n(E)-ik(E)$, as a function of photon energy E, for crystalline semiconductors and dielectrics is developed based on our previous derivation of $N(E)$ for amorphous materials. The extinction coefficient $k(E)$ is deduced from a one-electron model with finite lifetime for the excited electron state. The refractive index $n(E)$ is then derived from the Kramers-Kronig relation as the Hilbert transform of $k(E)$. It is shown that $n(\infty)>1$. Excellent agreement is found between our equations for $n(E)$ and $k(E)$ and published measured values for crystalline Si, Ge, GaP, GaAs, GaSb, InP, InAs, InSb, SiC, cubic C, and α-SiO$_2$, over a wide range of energies ($\sim$0–20 eV). Far fewer parameters, all of which have physical significance, are required and they can be determined for a particular material from the position and strength of the peaks in the k spectrum.

I. INTRODUCTION

Optical properties of any medium can be described by the complex index of refraction, $N=n-ik$, or the complex dielectric function, $\epsilon=\epsilon_1-i\epsilon_2$. ϵ is related to N by $\epsilon=N^2$, so that ϵ_1 and ϵ_2 can be determined from a knowledge of n and k: $\epsilon_1=n^2-k^2$ and $\epsilon_2=2nk$. The real and imaginary parts of the complex index of refraction, n and k, are termed the refractive index and the extinction coefficient, respectively. In addition to k and ϵ_2, which relate to absorption of light, the absorption coefficient, $\alpha=2\omega k/c$, is used to describe absorption. ω represents the photon frequency and c the speed of light. n and k, ϵ_1 and ϵ_2, and α are referred to as the optical constants of the medium. Values of the optical constants depend on the photon energy, $E=\hbar\omega$, i.e., $N=N(E)=n(E)-ik(E)$, $\epsilon=\epsilon(E)=\epsilon_1(E)-i\epsilon_2(E)$, and $\alpha=\alpha(E)$. These functions are called optical dispersion relations.

Previous formulations of optical dispersion relations for crystalline semiconductors and dielectrics are complicated.[1–4] Optical constants are determined in closed analytical form only for a narrow range of photon energies just above the energy-band gap, E_g, i.e., for the absorption edge. In this range it is argued that α as well as k and ϵ_2 (since n is assumed constant for $E\approx E_g$) can be broken into two parts. For $\alpha<\alpha_0$ (where α_0 represents some experimentally determined cutoff value), an empirical exponential dependence on E, referred to as Urbach's tail, is assumed.[5] For $\alpha>\alpha_0$, a power-law dependence on E is derived, based on a one-electron model with infinite lifetime for the excited electron state. The value of the exponent depends on the type of transition: direct, forbidden, or indirect.[2]

Beyond the absorption edge, optical constants are not determined in closed analytical form. Analysis of critical points in the Brillouin zone plays a major role in their determination.[1,3] For example, an edge in the ϵ_2 versus E spectrum is attributed to a transition corresponding to $\hbar\omega=E_{cv}(\mathbf{k}_{\text{crit}})$.[1] At a critical point, $\mathbf{k}=\mathbf{k}_{\text{crit}}$, the function $E_{cv}(\mathbf{k})=E_c(\mathbf{k})-E_v(\mathbf{k})$ is an extremum. ($\mathbf{k}$ represents electron wave vector and indices c and v represent conduction and valence bands, respectively.) A peak in ϵ_2 versus E is attributed to a transition corresponding to an accidental pairing of two critical points occurring near the same energy (sometimes enhanced by exciton interactions).[1] A typical assignment of critical-point transitions to the major peaks and edges in $\epsilon_2(E)$ for Ge is given by Brust, Philip, and Bassani, based on pseudopotential calculations.[1,3] (See Sec. III.)

The principle of causality[6] leads to a fundamental relation between the real, $n(E)$, and imaginary, $k(E)$, parts of $N(E)$, the Kramers-Kronig relation. Thus, theoretically, when k as a function of E is known, $n(E)$ can be determined. However, except for harmonic-oscillator fits to the measured data,[7] formulations of $n(E)$ do not relate it to $k(E)$. Instead, $n(E)$ is determined empirically by fitting data to various model equations.[4] Commonly used are Sellmeier-type equations or equations involving a sum of Sellmeier terms, all valid for a limited range of energies. The particular equation applied to a given material is determined by the resulting fit it gives to measured data.[4]

When an oscillator fit is used, n can be related to k through the Kramers-Kronig relation. However, k cannot be correctly described at the absorption edge since the energy-band gap is not incorporated into an oscillator model. In addition many fitting parameters are required. For example, 22 parameters are used to describe n and k for Si in the 0–10-eV range.[7]

In this paper we present a new formulation for the complex index of refraction of crystalline semiconductors

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and dielectrics. We deduce an expression for $k(E)$ based on a one-electron model which includes a finite lifetime of the excited electron state, extending our recent derivation for amorphous materials.[8] The need to invoke an accidental degeneracy of two critical points in order to account for peaks is eliminated in the present treatment. A peak in the k-versus-E spectrum can be attributed to a transition corresponding to $\hbar\omega = E_c(\mathbf{k}_{\text{crit}}) - E_v(\mathbf{k}_{\text{crit}})$. We then derive $n(E)$ from $k(E)$ via the Kramers-Kronig relation. We deduce that $n(E)$ approaches a value greater than one in the limit that E approaches infinity, in contrast to the classical theory of dispersion where $n(\infty)=1$.

The resulting expressions simultaneously provide excellent fits to the measured and published n and k values of a large number of materials (so far eleven) over a wide range of photon energies in the fundamental region (~ 0 to 20 eV), with far fewer parameters (all of which have physical significance) than other treatments. In the fundamental region, the energy ranges from the lowest absorption edge up to an energy where no more structure is observable.[1]

Finally, when other optical constants such as $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, as well as normal-incidence reflectance,

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} ,$$

are expressed in terms of these new equations for $k(E)$ and $n(E)$, we show that excellent fits to experimental data are obtained.

II. NEW FORMULATION OF $n(E)$ AND $k(E)$

This formulation of $N(E)$ for crystalline semiconductors and dielectrics is based on our previous derivation of $n(E)$ and $k(E)$ for amorphous semiconductors.[8] We deduced an expression for $\alpha(\omega)$, the absorption coefficient, for the amorphous case, by considering electron transitions between two energy bands due to photon absorption. $\alpha(\omega)$ was defined to be[8]

$$\alpha = \frac{\Phi\Theta}{I_0} , \tag{1}$$

where $\Phi(\omega)$ is the energy absorbed in the frequency range ω to $\omega + d\omega$ per unit time, Θ is the number of possible transitions per unit volume in a layer of thickness Δx, and I_0 is the incident photon intensity.

Assuming that the excited state to which the electron transfers has a finite lifetime τ, $\Phi(\omega)$ is given by

$$\Phi(\omega) = \frac{8\pi^2}{3\hbar c} e^2 \omega I_0 \, | \langle b | \mathbf{x} | a \rangle |^2 \times \frac{\hbar^2 \gamma}{2\pi(E_b - E_a - \hbar\omega)^2 + \hbar^2\gamma^2/4} , \tag{2}$$

where $| a \rangle$ represents the initial state of energy E_a, $| b \rangle$ represents the final state of energy E_b, and $\gamma = 1/\tau$. From Eq. (2) it is seen that $\Phi(\omega)$ is a maximum when $\hbar\omega = E_b - E_a$.

In amorphous semiconductors the valence and conduction bands are thought to arise from a broadening of bonding, $| \sigma \rangle$, and antibonding, $| \sigma^* \rangle$, molecular-orbital states when the solid is formed.[9] We assumed that $\Phi(\omega)$ is a maximum, when $\hbar\omega = E_{\sigma^*} - E_\sigma$. Therefore, Eq. (2) can be written as

$$\Phi(\omega) = \frac{8\pi^2}{3\hbar c} e^2 \omega I_0 \, | \langle \sigma^* | \mathbf{x} | \sigma \rangle |^2 \times \frac{\hbar^2 \gamma}{2\pi(E_{\sigma^*} - E_\sigma - \hbar\omega)^2 + \hbar^2\gamma^2/4} . \tag{3}$$

Assuming a $\frac{1}{2}$ power law for the densities of states in the valence and conduction bands,

$$\Theta \propto (\hbar\omega - E_g)^2 . \tag{4}$$

Inserting Eqs. (3) and (4) into (1) and using $k = \alpha c / 2\omega$,

$$k = \text{const} \times \frac{2\pi}{3} e^2 \hbar^2 \, | \langle \sigma^* | \mathbf{x} | \sigma \rangle |^2 \times \frac{\gamma}{(E_{\sigma^*} - E_\sigma - \hbar\omega)^2 + \hbar^2\gamma^2/4} (\hbar\omega - E_g)^2 . \tag{5}$$

Therefore, for amorphous semiconductors and dielectrics,

$$k(E) = \frac{A}{E^2 - BE + C} (E - E_g)^2 , \tag{6}$$

where

$$A = \text{const} \times | \langle \sigma^* | \mathbf{x} | \sigma \rangle |^2 \gamma , \tag{7}$$

$$B = 2(E_{\sigma^*} - E_\sigma) , \tag{8}$$

$$C = (E_{\sigma^*} - E_\sigma)^2 + \frac{\hbar^2\gamma^2}{4} . \tag{9}$$

As mentioned in the Introduction, when k as a function of E is given, $n(E)$ can be found. The principle of causality leads to a relation between $n(E)$ and $k(E)$, the Kramers-Kronig relation.[6] This principle (sometimes referred to as the principle of limiting distance[10]) states that no signal ever precedes the light cone of its source. When this principle is satisfied, $N(E)$ will be analytic (regular) in the lower half plane. (Using the convention $N = n + ik$, N is analytic in the upper half plane.) Conversely, if $N(E)$ is analytic in the lower half plane, causality is satisfied. As a result, $n(E)$ is determined as the Hilbert transform of $k(E)$. If $k(E)$ tends toward a constant as $E \to \infty$, the values of $k(\infty)$ and $n(\infty)$ must be subtracted out from the Hilbert transform, so that

$$n(E) - n(\infty) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{k(E') - k(\infty)}{E' - E} dE' , \tag{10}$$

where P denotes Cauchy's principle value integral. [As discussed later on, $n(\infty) > 1$.]

The refractive index, $n(E)$, is then found using Eq. (10):

$$n(E) - n(\infty) = \frac{B_0 E + C_0}{E^2 - BE + C} , \tag{11}$$

where

$$B_0=\frac{A}{Q}\left[-\frac{B^2}{2}+E_gB-E_g^2+C\right], \quad (12)$$

$$C_0=\frac{A}{Q}\left[(E_g^2+C)\frac{B}{2}-2E_gC\right], \quad (13)$$

$$Q=\tfrac{1}{2}(4C-B^2)^{1/2}. \quad (14)$$

These dispersion relations for $n(E)$ and $k(E)$ closely fit the published data for a wide variety of amorphous materials, such as a-Si, a-Si:H, a-$\mathrm{Si_3N_4}$, and a-$\mathrm{TiO_2}$, over a wide range of photon energies.[8]

In crystalline semiconductors and dielectrics, long-range order gives rise to structure in $k(E)$ containing several peaks, in contrast to a single peak in $k(E)$ for the amorphous case. In order to account for these peaks, we first note that in the amorphous case the maximum for $\Phi(\omega)$, which occurs when $\hbar\omega\simeq E_{\sigma^*}-E_\sigma=B/2$, is very close to the maximum for $k(E)$.[8] Thus we assume a peak in the k spectrum of crystalline semiconductors and dielectrics occurs when the energy absorbed in a transition, $\Phi(\omega)$, has a local maximum (approximately); in which case we assume that the transition corresponds to

$$\hbar\omega\approx E_c(\mathbf{k}_{\mathrm{crit}})-E_v(\mathbf{k}_{\mathrm{crit}}).$$

When $\mathbf{k}=\mathbf{k}_{\mathrm{crit}}$, then $\nabla_{\mathbf{k}}E_{cv}(\mathbf{k}_{\mathrm{crit}})=0$. This condition is satisfied, for the most part, at symmetry points, or symmetry lines or planes in the Brillouin zone.[1,11] Therefore, analogous to previous treatments,[1,3,11] symmetry analysis of the Brillouin zone of these materials should determine which specific states are involved in transitions which produce peaks in $k(E)$. In this paper we do not assign any particular states to these transitions.

Thus, we take $\Phi(\omega)$ as a sum of terms, each term having the form given by Eq. (3), where the number of terms is equal to the number of peaks in $k(E)$. The extinction coefficient for crystalline materials is then given by

$$k(E)=\left[\sum_{i=1}^{q}\frac{A_i}{E^2-B_iE+C_i}\right](E-E_g)^2 \quad (q=\text{integer}), \quad (15)$$

where

$$A_i=\text{const}\times|\langle\psi^c_{\mathrm{crit}}|\mathbf{x}|\psi^v_{\mathrm{crit}}\rangle|_i^2\gamma_i, \quad (16)$$

$$B_i=2[E_c(\mathbf{k}_{\mathrm{crit}})-E_v(\mathbf{k}_{\mathrm{crit}})]_i, \quad (17)$$

$$C_i=[E_c(\mathbf{k}_{\mathrm{crit}})-E_v(\mathbf{k}_{\mathrm{crit}})]_i^2+\frac{\hbar^2\gamma_i^2}{4}. \quad (18)$$

In Eq. (16), $\psi^{c,v}_{\mathrm{crit}}$ denotes the electron state in the conduction or valence band when $\mathbf{k}=\mathbf{k}_{\mathrm{crit}}$.

Taking the total number of possible transitions per unit volume, Θ, proportional to $(E-E_g)^2$ in Eq. (15), implies that the density of states in valence and conduction bands, $\eta_v(E)$ and $\eta_c(E)$, follow a $\frac{1}{2}$ power law. This approximation ignores the discontinuities in the slopes of η_v and η_c occurring at critical points in the Brillouin zone. It amounts to taking a smoothed-out average of the true η's in calculating Θ. See Fig. 1. The justification of this approximation can only be ascertained from the fit of Eq. (15) to experimental data. Further remarks will be presented in a future work.

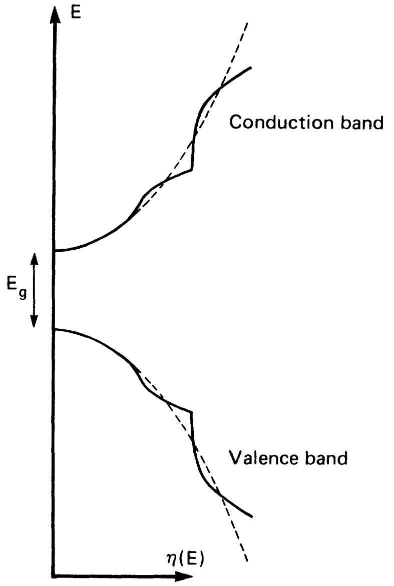

FIG. 1. The solid line schematically depicts discontinuities in the slope of the density of states $\eta_v(E)$ and $\eta_c(E)$ occurring at critical points. The dashed line shows that a $\frac{1}{2}$ power-law behavior for $\eta_v(E)$ and $\eta_c(E)$ constitutes a smoothed-out average of the above.

The refractive index, $n(E)$, determined from Kramers-Kronig analysis as the Hilbert transform of Eq. (15), will then be given by

$$n(E)=n(\infty)+\sum_{i=1}^{q}\frac{B_{0_i}E+C_{0_i}}{E^2-B_iE+C_i} \quad (q=\text{integer}), \quad (19)$$

where

$$B_{0_i}=\frac{A_i}{Q_i}\left[-\frac{B_i^2}{2}+E_gB_i-E_g^2+C_i\right], \quad (20)$$

$$C_{0_i}=\frac{A_i}{Q_i}\left[(E_g^2+C_i)\frac{B_i}{2}-2E_gC_i\right], \quad (21)$$

$$Q_i=\tfrac{1}{2}(4C_i-B_i^2)^{1/2}. \quad (22)$$

In both the amorphous and crystalline case we do not assume that $n(\infty)=1$, in contrast to classical dispersion theory. In fact, Toll has shown[10] that mathematics dictates that $n(\infty)=1+ca$, where c represents the speed of light and the factor a represents a positive constant, when the condition of causality as well as the condition $k(E)\rightarrow0$ as $E\rightarrow\infty$ are satisfied. Assuming these two conditions, and using the convention that $N(E)=n(E)+ik(E)$ [which gives $N(E)$ analytic in the upper half plane], he derives the following dispersion relation:

$$N(\omega_r)=1+ca+\frac{c}{\pi}\lim_{\omega_i\to 0+}\int_0^{\infty}\frac{\alpha(\omega_r')d\omega_r'}{\omega_r'^2-(\omega_r+i\omega_i)^2}\,, \tag{23}$$

where ω_r and ω_i are the real and imaginary parts of the complex frequency $\omega=\omega_r+i\omega_i$ and α is the absorption coefficient.

Substituting for $k(E)$ in the above equation (23) gives

$$N(\omega_r)=1+ca+\frac{1}{\pi}\lim_{\omega_i\to 0+}\int_{-\infty}^{\infty}\frac{k(\omega_r')d\omega_r'}{\omega_r'-\omega_r+i\omega_i}\,, \tag{24}$$

which is equivalent to

$$n(E)=1+ca+\frac{1}{\pi}\mathrm{P}\int_{-\infty}^{\infty}\frac{k(E')dE'}{E'-E}\,. \tag{25}$$

Toll interprets the term ca in Eq. (25) as arising from an absorption line at infinity.[12] This term may seem physically implausible, since the condition that $k(E)\to 0$ as $E\to\infty$ is incorporated; however, as Toll points out, the term is "logically permitted by the principle of limiting distances. . . . Mathematical deduction does not exclude this term. It has to be explicitly excluded on other grounds."

Toll's derivation for $n(\infty)=1+ca$ can trivially be extended to the case at hand where the principle of limiting distance is satisfied but $k(E)\to$constant as $E\to\infty$. A subtraction of $k(\infty)$ in the integral of Eq. (25) is all that is needed so that

$$n(E)=1+ca+\frac{1}{\pi}\mathrm{P}\int_{-\infty}^{\infty}\frac{[k(E')-k(\infty)]dE'}{E'-E}\,, \tag{26}$$

giving $n(\infty)=1+ca>1$ in this more general case. Given that $k(\infty)\neq 0$, it would seem illogical to exclude the term ca on physical grounds, since $n(\infty)=1$ implies no interaction for $E\to\infty$. Thus, $n(\infty)$ is greater than one because there is absorption in the limit $E\to\infty$.

III. EXPERIMENTAL VERIFICATION

In this section we will apply Eqs. (15) and (19) to published experimental data. It will be shown that these equations describe, over a wide range of photon energies, the optical constants of a large number of crystalline semiconductor and dielectric materials. We will also show that the real, $\epsilon_1(E)=n^2(E)-k^2(E)$, and imaginary, $\epsilon_2(E)=2n(E)k(E)$, parts of the complex dielectric function, $\epsilon(E)=\epsilon_1(E)-i\epsilon_2(E)$, as well as normal-incidence reflectance spectrum,

$$R(E)=\frac{[n(E)-1]^2+k^2(E)}{[n(E)+1]^2+k^2(E)}\,,$$

can be described when $n(E)$ and $k(E)$ are given by Eqs. (15) and (19).

A. The data

Measured values of the optical constants of many materials, reported by different investigators, are compiled in Ref. 4. However, as pointed out by Aspnes and Studna,[13] discrepancies of the order of 10–30% are common in "seemingly equally valid" data.

For the present study, we selected crystalline solids for which n and k were available in tabulated form, for a relatively wide range of energies, measured in the same laboratory. This provided a measure of consistency. The selected crystalline solids are group IV semiconductors (Si and Ge), group III-V semiconductors (GaP, GaAs, GaSb, InP, InAs, and InSb), group IV-IV semiconductor (SiC), and crystalline insulators (cubic C and α-SiO$_2$).

The optical constants for Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb, in the 1.5–6.0-eV range, are by Aspnes and Studna.[13] Beyond this range (and sometimes overlapping at end points) data for some of these materials from other sources[4] were also included. This was done mainly to include large peaks in k spectrum and also to elucidate discrepancies.

Experimental data for SiC (~5 to 13 eV), cubic C (~5 to 18 eV), and α-SiO$_2$ (~2 to 18 eV) are by Leveque and Lynch,[14] Philipp and Taft,[15] and Philipp,[16] respectively.

B. The band gap, E_g

The values of E_g for various materials quoted in the literature are obtained, usually, by extrapolating the "linear" portion of the plot of $(\alpha\hbar\omega)^{1/m}$ versus $\hbar\omega$, where $m=\frac{1}{2}$, $\frac{3}{2}$, or 2, depending on the assumed mode of optical transition (allowed direct, forbidden, or indirect, respectively). The quoted value of E_g (say, at room temperature) for a given semiconductor may thus vary depending on the method of extrapolation and mode of transition. For example, for Ge, Dash and Newman[17] placed the indirect threshold transition at 0.62 eV and the direct tran-

TABLE I. Values of the parameters A_i, B_i, C_i, and $n(\infty)$ for crystalline SiC, obtained by least-square fitting of experimental n and k data to Eqs. (19) and (15), taking the number of terms equal to either 1, 2, or 4. The energy-band gap of SiC is also given. The corresponding theoretical plots of $n(E)$ and $k(E)$ are shown in Fig. 2.

	A_i	B_i (eV)	C_i (eV^2)	$n(\infty)$	E_g (eV)
1 term	0.259 26	14.359	53.747	1.680	2.50
2 terms	0.180 28	14.222	52.148	1.337	
	0.107 00	19.397	99.605		
4 terms	0.001 08	13.227	43.798	1.353	
	0.190 54	14.447	53.860		
	0.006 46	19.335	94.105		
	0.053 66	21.940	125.443		

sition at 0.81 eV, whereas E_g is given as 0.66 eV in Ref. 18 and 0.67 eV in Ref. 19. For Si, E_g is cited to be 1.06 eV,[17] 1.08 eV,[18] and 1.11 eV.[2] For GaAs, E_g is cited as 1.39 eV,[19] 1.4 eV,[18] and 1.43 eV.[2]

In our formulation, E_g specifies the position of absolute minimum in k spectrum. Experimentally, the absolute minimum occurs at the onset of the "fundamental" absorption edge (e.g., see the k spectra for various crystalline semiconductors and dielectrics in Ref. 4). Thus we have taken E_g (listed in Tables I, II, and III) as such.

C. The curve fitting program

A nonlinear least-square curve-fitting computer program was used to obtain the parameters A_i, B_i, and C_i, and $n(\infty)$, by minimizing the sum of the square of differences of experimental and theoretical n and k simultaneously, subject to the following constraints:

$$A_i,\ B_i,\ C_i,\ n(\infty),\ \text{and}\ 4C_i - B_i^2 > 0\ .$$

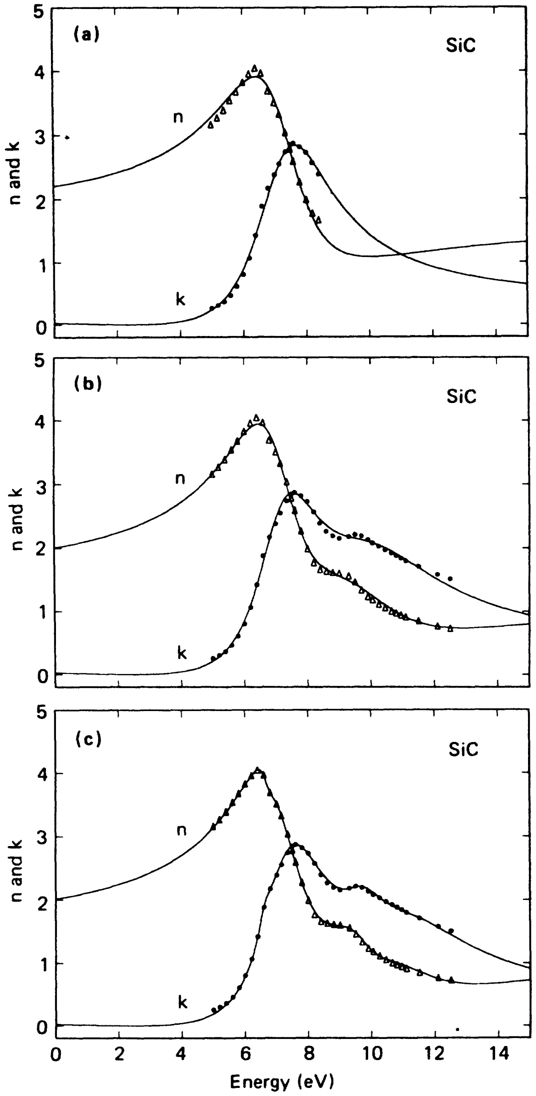

FIG. 2. The solid lines are the theoretical plots of $n(E)$ and $k(E)$ given by Eqs. (19) and (15) with the parameters specified in Table I for crystalline SiC, taking the number of terms equal to 1, 2, and 4 in (a), (b), and (c), respectively. In (a) only experimental data in the 5–8.5-eV range are considered. n: △ and k: ● experimental data are by Leveque and Lynch (Ref. 14).

Reasonable initial guesses of the parameters are needed in running a nonlinear least-squares curve-fitting program. Since k is close to a local maximum when

$$\hbar\omega = [E_c(\mathbf{k}_{\text{crit}}) - E_v(\mathbf{k}_{\text{crit}})]_i$$

the position of the ith peak in k spectrum, E_i^{peak}, provides an initial guess for B_i:

$$B_i \simeq 2E_i^{\text{peak}} \quad (i=1,\ldots,q)\ .$$

It can then be shown that

$$C_i \simeq (E_i^{\text{peak}})^2 \quad (i=1,\ldots,q)\ .$$

An approximate value for A_i can be obtained by the knowledge of the magnitude of the peaks. The initial guess for $n(\infty)$ for all materials studied was chosen as unity.

D. Results

Figures 2–9 demonstrate that Eqs. (15) and (19) describe optical properties of a large number of materials.

1. The number of terms

Each term in the sum for k in Eq. (15) contributes a peak to the k spectrum and a corresponding peak to n. In principle, the number of terms in our formulation, i.e., the integer q, thus equals the number of peaks in k. In practice, however, n and k are known for a limited range of energies, in which case q is taken as the number of peaks discernable in that range. In addition, shoulders and doublets contribute to the number of terms. As an example, consider the experimentally determined optical constants of SiC in the 5–8.5-eV range as depicted in Fig. 2(a). In this range, one dominant peak in k, at 7.6 eV, is present. Taking the number of terms equal to one ($q=1$) and $E_g=2.5$ eV, the parameters specified in Table I are obtained. Thus, as seen in Fig. 2(a), the optical constants of SiC in the 5–8.5-eV range are described quite well by only five parameters.

Now, consider the 5–13-eV range, as depicted in Fig. 2(b). Two prominent peaks in k at 7.6 and 9.5 eV are present. Taking the number of terms equal to two, we then obtain the parameters specified in Table I. The corresponding theoretical plots of $n(E)$ and $k(E)$ are shown in Fig. 2(b). As seen in this figure, although eight parameters give essentially all the notable features of n and k for cyrstalline SiC in the 5–13-eV range, a still better fit can be obtained by taking into account the shoulders at approximately 6 and 11 eV, i.e., taking $q=4$. This is shown in Fig. 2(c). Therefore, as the number of terms decreases, the smaller peaks disappear and eventually only the main peak remains, resembling the amorphous state of the semiconductor.

It is seen in Table I that as the number of terms

TABLE II. Values of the parameters A_i, B_i, C_i, and $n(\infty)$ for different crystalline materials, obtained by least-square fitting of experimental n and k data to Eqs. (19) and (15), taking the number of terms equal to 4. The energy-band gaps of these materials are also given. The corresponding theoretical plots of $n(E)$ and $k(E)$ are shown in Figs. 3–5. The theoretical plots of $\epsilon_2(E)$ for Ge, and $\epsilon_1(E)$ and $\epsilon_2(E)$ for Si, are shown in Figs. 6(a) and 7.

	A_i	B_i (eV)	C_i (eV^2)	$n(\infty)$	E_g (eV)
Si	0.004 05	6.885	11.864	1.950	1.06
	0.014 27	7.401	13.754		
	0.068 30	8.634	18.812		
	0.174 88	10.652	29.841		
Ge	0.085 56	4.589	5.382	2.046	0.60
	0.218 82	6.505	11.486		
	0.025 63	8.712	19.126		
	0.077 54	10.982	31.620		
GaP	0.006 52	7.469	13.958	2.070	2.17
	0.144 27	7.684	15.041		
	0.139 69	10.237	26.567		
	0.005 48	13.775	47.612		
GaAs	0.000 41	5.871	8.619	2.156	1.35
	0.200 49	6.154	9.784		
	0.096 88	9.679	23.803		
	0.010 08	13.232	44.119		
GaSb	0.002 68	4.127	4.267	1.914	0.65
	0.340 46	4.664	5.983		
	0.086 11	8.162	17.031		
	0.026 92	11.146	31.691		
InP	0.202 42	6.311	10.357	1.766	1.27
	0.023 39	9.662	23.472		
	0.030 73	10.726	29.360		
	0.044 04	13.604	47.602		
InAs	0.184 63	5.277	7.504	1.691	0.30
	0.009 41	9.130	20.934		
	0.052 42	9.865	25.172		
	0.034 67	13.956	50.062		
InSb	0.002 96	3.741	3.510	1.803	0.12
	0.221 74	4.429	5.447		
	0.060 76	7.881	15.887		
	0.045 37	10.765	30.119		
Cubic *C*	0.105 25	15.027	56.859	1.419	6.00
	0.086 04	18.506	87.212		
	0.149 45	23.736	142.794		
	0.044 72	31.468	253.515		
α-SiO_2	0.008 67	20.729	107.499	1.226	7.00
	0.029 48	23.273	136.132		
	0.019 08	28.163	199.876		
	0.017 11	34.301	297.062		

TABLE III. Values of the parameters A_i, B_i, C_i, and $n(\infty)$ for crystalline Ge, obtained by least-squares fitting of experimental n and k data to Eqs. (19) and (15), taking the number of terms equal to 5. The energy band gap of Ge is also given. The corresponding theoretical plots of $n(E)$, $k(E)$, and $R(E)$ are shown in Figs. 8 and 9(b).

	A_i	B_i (eV)	C_i (eV^2)	$n(\infty)$	E_g (eV)
Ge	0.001 03	4.313	4.654	2.161	0.60
(5 terms)	0.116 37	4.677	5.639		
	0.109 68	6.728	11.858		
	0.034 79	8.704	19.119		
	0.077 11	11.056	31.879		

changes, the values of the parameters are slightly modified, as expected. However, the modifications of B and C are surprisingly small, and it is only the parameter A (which determines the strength of each term) that significantly changes.

As will be shown in the following subsection, generally four terms are sufficient to describe n and k over a wide spectral range, indicating four dominant critical point transitions. Nevertheless, in some cases more than four terms may be required to bring out the details of the spectra.

2. *Examples*

Taking the number of terms equal to 4, corresponding to 4 "easily" discernible peaks, Table II contains the pa-

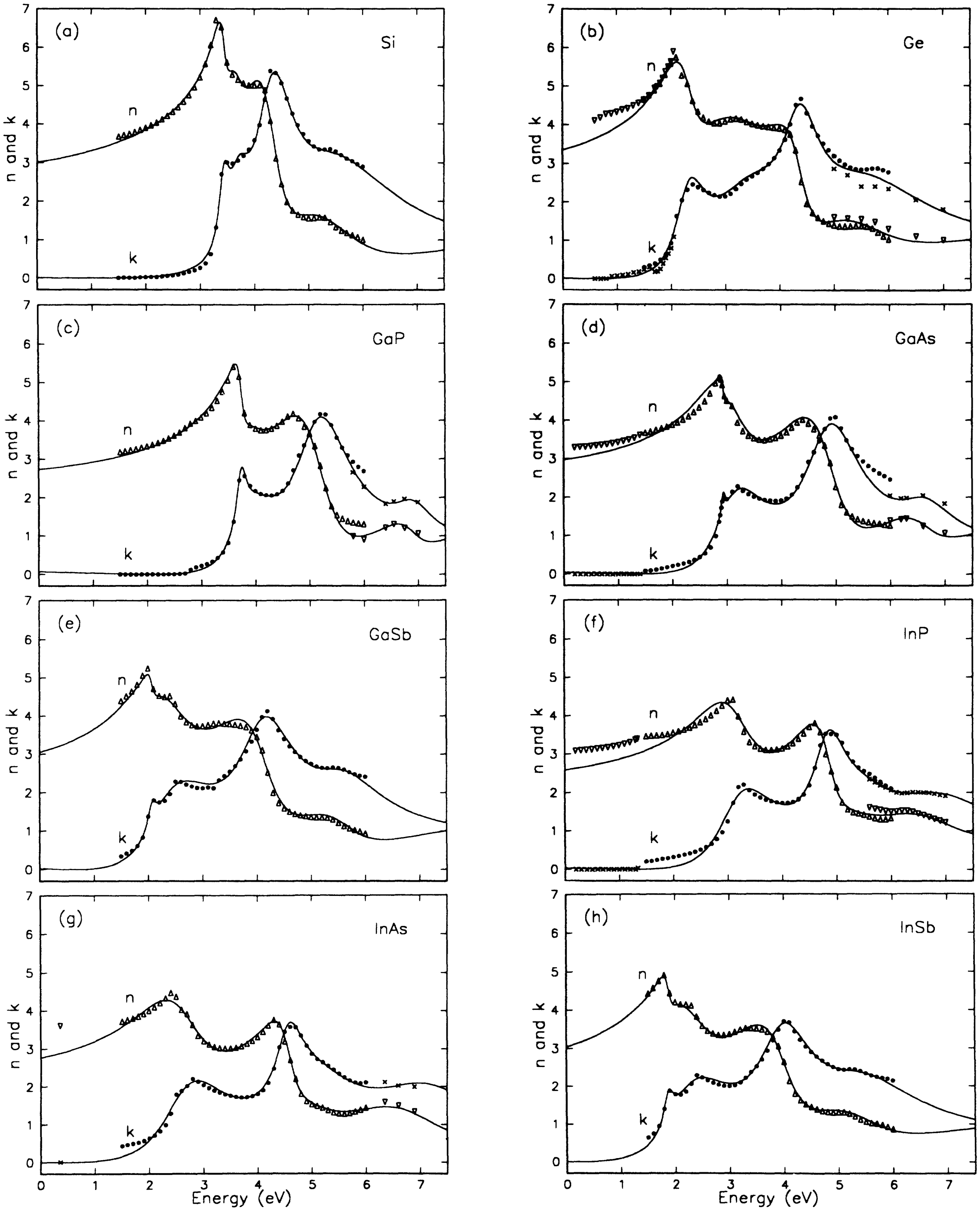

FIG. 3. The solid lines are the theoretical plots of $n(E)$ and $k(E)$ given by Eqs. (19) and (15) with the parameters specified in Table II for crystalline Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb. n: △ and k: ● experimental data are from Aspnes and Studna (Ref. 13). n: ∇ and k: × experimental data are from Ref. 4.

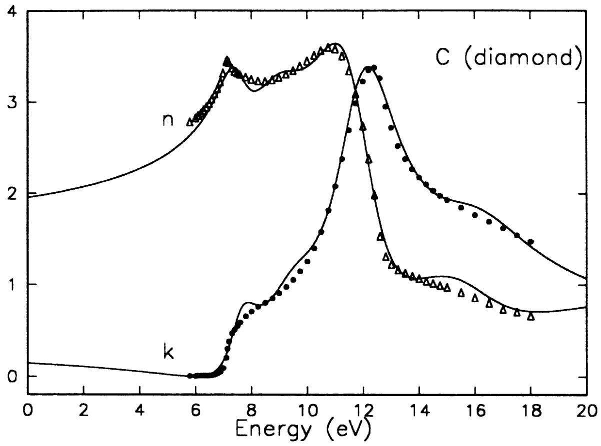

FIG. 4. The solid lines are the theoretical plots of $n(E)$ and $k(E)$ given by Eqs. (19) and (15) with the parameters specified in Table II for crystalline cubic *C*. *n*: △ and *k*: ● experimental data are by Philipp and Taft (Ref. 15).

rameters A_i, B_i, C_i, and $n(\infty)$ for different materials, determined by the least-square fitting program. In agreement with the discussion in Sec. II, $n(\infty)$ was found to be greater than one, the actual value depending on the material. Notice that B_i's are very close to $2E_i^{\text{peak}}$. For instance, for α-SiO$_2$, experimentally the peaks in k occur at 10.45, 11.7, 14.3, and 17.25 eV,[16] which are very close to the $B_i/2$ values in Table II at 10.36, 11.64, 14.08, and 17.15 eV.

If the formulas for n and k are given, then the real and imaginary parts of the complex dielectric constant are known. For example, Fig. 6(a) shows a plot of $\epsilon_2 = 2nk$ for Ge, with the parameters specified in Table II. As seen in this figure, a much better correspondence exists between the experimental data and our formulation than the previous pseudopotential approach of Brust, Phillips, and Bassani[20,21] shown in Fig. 6(b). Another example is shown in Fig. 7, depicting the excellent agreement between the present formulation and the experimental ϵ_1 and ϵ_2 of Si.

It appears that the reflectance spectrum provides a better guidance for determining the number of terms because structure is more readily discernable in measured $R(E)$ than in measured $k(E)$, since k is found experimentally from information contained in the reflected beam. For instance, in the 0–27-eV range, the measured R for Ge by Philipp and Ehrenreich[22,23] contains a doublet (at ~2.1 and 2.3 eV), a shoulder (at ~3.5 eV), and two well-defined peaks (at ~4.5 and 5.5 eV). See Fig. 9(a). Thus, taking the number of terms equal to 5 (in-

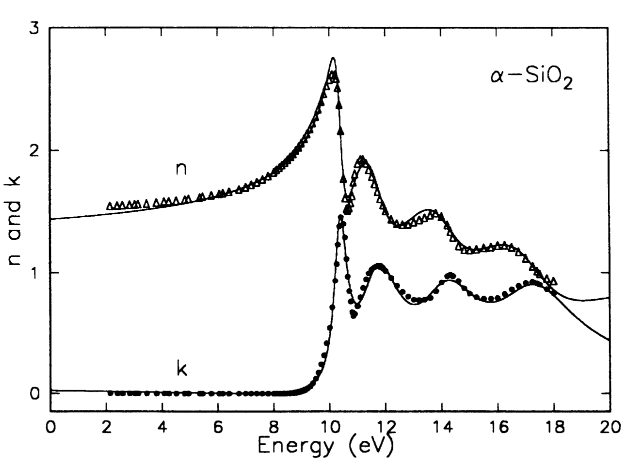

FIG. 5. The solid lines are the theoretical plots of $n(E)$ and $k(E)$ given by Eqs. (19) and (15) with the parameters specified in Table II for crystalline α-SiO$_2$. *n*: △ and *k*: ● experimental data are by Philipp (Ref. 16).

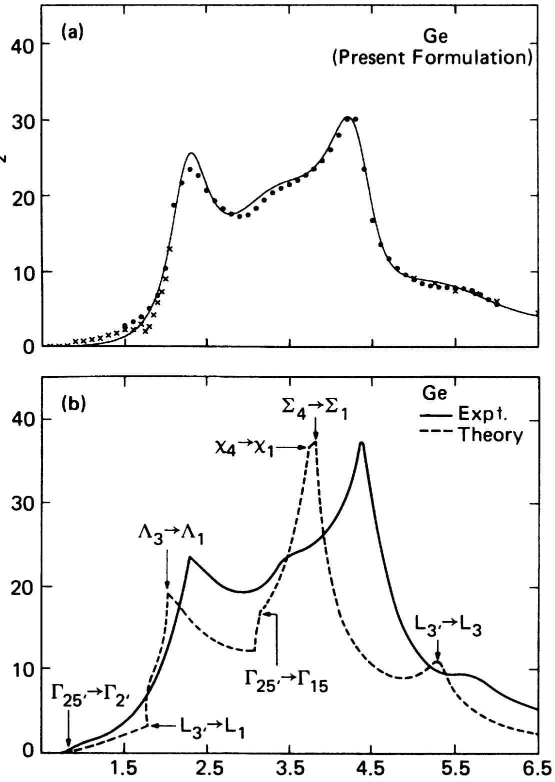

FIG. 6. (a) The solid line is the theoretical plot of $\epsilon_2(E) = 2n(E)k(E)$, where $n(E)$ and $k(E)$ are given by Eqs. (19) and (15) with the parameters specified in Table II for crystalline Ge. The experimental ϵ_2 data ● and × are from Aspnes and Studna (Ref. 13) and Ref. 4, respectively. (b) Pseudopotential calculation of ϵ_2 for Ge by Brust, Phillips, and Bassani (Refs. 20 and 21). A typical assignment of critical-point transitions to the major peaks and edges is shown. The 4.5-eV peak is attributed to the accidental degeneracy of an M_1 edge due to the $X_4 \rightarrow X_1$ transition and an M_2 edge due to the $\Sigma_4 \rightarrow \Sigma_1$ transition. The 2.1-eV edge is attributed to an M_1 critical point due to the $\Lambda_3 \rightarrow \Lambda_1$ transition. Excitonlike effects (electron-hole interactions), causing line narrowing, are attributed to these transitions. The edge at 0.8 eV (argued to be a direct threshold) is attributed to an M_0 edge due to the $\Gamma_{25'} \rightarrow \Gamma_{2'}$ transition. The notation for the edges M_0, M_1, M_2 is detailed in Refs. 1 and 3, while the notation for the states of X, Σ, Γ, is detailed in Refs. 1 and 11.

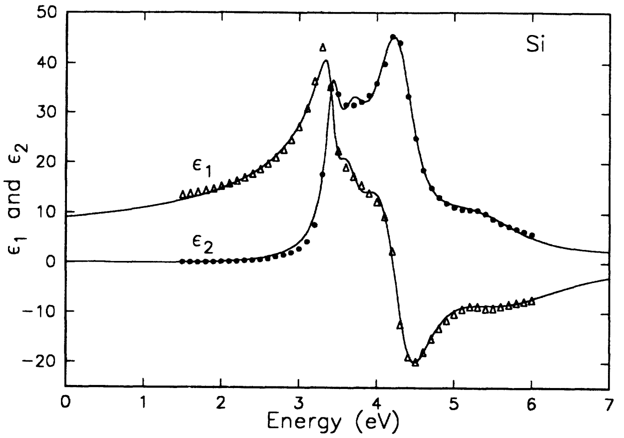

FIG. 7. The solid lines are the theoretical plots of $\epsilon_1(E)=n^2(E)-k^2(E)$ and $\epsilon_2(E)=2n(E)k(E)$, where $n(E)$ and $k(E)$ are given by Eqs. (19) and (15) with the parameters specified in Table II for crystalline Si. ϵ_1: △ and ϵ_2: ● experimental data are from Aspnes and Studna (Ref. 13).

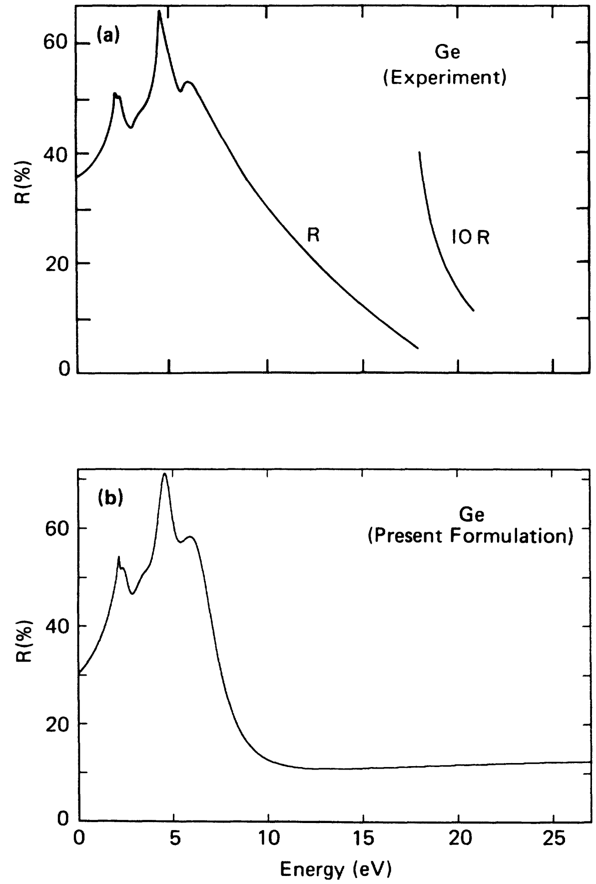

FIG. 9. (a) Experimental reflectance spectrum of crystalline Ge taken from Ref. 22. (b) Theoretical reflectance spectrum, $R(E)=\{[n(E)-1]^2+k^2(E)\}/\{[n(E)+1]^2+k^2(E)\}$, where $n(E)$ and $k(E)$ are given by Eqs. (19) and (15) with the parameters specified in Table III for crystalline Ge.

stead of 4) should result in a better fit, bringing out the details of n and k at around 2 eV. This is seen in Fig. 8. The parameters so determined by the nonlinear curve-fitting to n and k are given in Table III. The corresponding theoretical R spectrum is plotted in Fig. 9(b), and can be compared with the measured spectrum shown in Fig. 9(a).

In Fig. 9, however, notice the poor fit between the theoretical and experimental reflectance spectra in the vacuum uv range ($E \gtrsim 7$ eV). We believe the reason for this is, in accordance with Philipp and Taft[24] and Aspnes,[25] the presence of a thin "native oxide" overlayer. This is because a thin oxide, exhibiting strong absorption in the vuv range, inevitably forms on the surface of most semiconductor materials upon exposure to atmosphere,[24,25] which in turn affects accurate reflectance measurements.

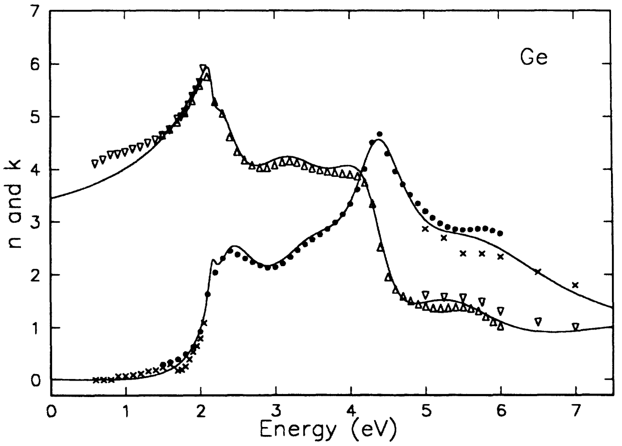

FIG. 8. The solid lines are the theoretical plots of $n(E)$ and $k(E)$ given by Eqs. (19) and (15) with the parameters specified in Table III for crystalline Ge. n: △ and k: ● experimental data are from Aspnes and Studna (Ref. 13). n: ▽ and k: × experimental data are from Ref. 4.

The dispersion relations developed in this paper, therefore, not only describe optical constants of crystalline semiconductors and dielectrics, but may also guide their accurate experimental determination.

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