

A generalized Cauchy dispersion formula and the refractivity of elemental semiconductors

To cite this article: D Y Smith *et al* 2001 *J. Phys.: Condens. Matter* **13** 3883

View the [article online](#) for updates and enhancements.

Related content

- [A new method for the determination of the optical mass of electrons in metals](#)
Bernd Hüttner
- [Optical spectra of thin In₂O₃ : Sn films](#)
D Mergel and Z Qiao
- [Two-level systems in fluorite mixed crystals](#)
S A FitzGerald, A J Sievers and J A Campbell

Recent citations

- [Tutorial: An introduction to terahertz time domain spectroscopy \(THz-TDS\)](#)
Jens Neu and Charles A. Schmuttenmaer
- [Silane Deposition via Gas-Phase Evaporation and High-Resolution Surface Characterization of the Ultrathin Siloxane Coatings](#)
Walid-Madhat Munief *et al*
- [Optical characterization of pore filling in mesoporous multilayers by ultrathin atomic layer deposited hafnium dioxide](#)
Andras Kovacs and Ulrich Mescheder



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

A generalized Cauchy dispersion formula and the refractivity of elemental semiconductors

D Y Smith^{1,2}, Mitio Inokuti¹ and William Karstens³

¹ Physics Division, Argonne National Laboratory, Argonne, IL 60439, USA

² Department of Physics, University of Vermont, Burlington, VT 05405, USA

³ Department of Physics, Saint Michael's College, Colchester, VT 05439, USA

Received 31 January 2001

Abstract

A generalized Cauchy dispersion formula applicable to both normal and anomalous dispersion in the refractive index of transparent materials is derived from the Kramers–Kronig relations. Several commonly used dispersion formulae are closely related to this result. The expansion coefficients, heretofore considered empirical, are simply the odd moments of the absorption spectrum. These ideas are illustrated for natural diamond, and high-purity silicon and germanium. Analysis of published data for these materials discloses extrinsic dispersive effects in the far infrared, even for ‘high-purity’ samples. We attribute this dispersion to free-carrier or defect-induced absorptions at energies below the range of measurements.

1. Introduction

Solid-state spectroscopies commonly involve measurement of either the absorptive or dispersive response of a material to an external probe [1]. In many instances, response theory provides simple sum-rule limitations on, and connections between, various measures of response [1–3]. Moreover, these limitations and connections are often independent of the details of the model used to describe the material and its interaction with the probe. Here we consider an instance of this involving Cauchy's 1830 elastic-ether theory of the refractive index [4, 5]. The present ideas developed during an extension [6] of self-consistent optical dispersion analysis [7] to semiconductors, but are also relevant to insulators.

A number of recent discussions [8, 9] of the refractive index, $n(\omega)$, of the semiconducting group IV elements have relied on fitting experimental data with Sellmeier [10] or Herzberger [11] dispersion formulae. The first of these has the form

$$n(\omega)^2 = 1 + \sum_i \frac{a_i \lambda^2}{\lambda^2 - \lambda_i^2} \quad (1)$$

with empirical parameters a_i and λ_i correspond to the strengths and resonant wavelengths of a model solid consisting of frictionless Lorentz oscillators [12]. This formula was originally derived by Sellmeier in 1871 [10] as an extension of Cauchy's theory of optical dispersion [4, 5]

to include the possibility of anomalous dispersion. Although this work was based on the ether theory, Maxwell's theory combined with Lorentz's model of the electronic response of matter leads to the same result [12].

The Herzberger dispersion formula [11],

$$n(\omega) = a + b\lambda^2 + \frac{c}{\lambda^2 - \lambda_0^2} + \frac{d}{(\lambda^2 - \lambda_0^2)^2} \quad (2)$$

may be viewed as an approximation to Sellmeier's result with a limited number of adjustable parameters, a , b , c , d , and λ_0 that was developed specifically for optical glasses in the visible and near infrared. These formulae, particularly Herzberger's, provide excellent practical interpolations for measured indices provided the wavelength regions near λ_i are avoided; however, the parameters involved are not directly related to fundamental properties of the material and have only a qualitative physical interpretation.

Here we demonstrate that Cauchy's original dispersion formula,

$$n(\omega) = n_0 + n_2\omega^2 + n_4\omega^4 + n_6\omega^6 \dots \quad \omega < \omega_h \quad (3)$$

where $\hbar\omega$ is the photon energy and $\hbar\omega_h$ is the lowest excitation threshold, follows directly from the Kramers–Kronig relations [13] for linear optical response, and that it may be generalized to include anomalous dispersion. Moreover, we show that the coefficients in our generalized Cauchy dispersion formula for the index are simply the odd energy moments of the material's absorption spectrum. Since our treatment is based on the analyticity of the complex refractive index, our generalized dispersion formula is linear in $n(\omega)$. In contrast, the Sellmeier formula, (1), has the added complication of being quadratic in $n(\omega)$ since its derivation depends directly on the analyticity of the dielectric response. These ideas are illustrated for the group IV elemental semiconductors, i.e. diamond, silicon and germanium. A by-product of our analysis is the finding that literature values of the infrared refractive index for these materials exhibit dispersion caused by extrinsic free carriers or defects absorbing in the sub-infrared, even for samples that were thought to be of 'high purity'.

2. Theory

Nonmetals display a region of high transparency for photons with energies between those for phonon or free-carrier absorption in the far infrared, and for interband electronic transition in the visible or near ultraviolet. At low temperatures, this region of high transparency extends to zero energy when phonon modes are infrared inactive, i.e. when dipole coupling to lattice modes is forbidden in first order by symmetry, as in defect-free, non-polar materials. Experimentally, the refractive index of such materials can be measured directly to high precision using traditional optical methods [14]. A simple connection between index measurements and other fundamental properties of the solid should therefore be valuable.

From the standpoint of linear-response theory, such a connection is provided by the Kramers–Kronig relations for the complex refractive index, $n(\omega) + i\kappa(\omega)$, where $n(\omega)$ is the refractive index and $\kappa(\omega)$ is the extinction coefficient. Specifically, in the absence of magnetic fields [15], the index is related to absorption at other energies by the Kramers–Kronig relation [13]

$$n(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega'. \quad (4)$$

Assuming transparency in the frequency range $\omega_l < \omega < \omega_h$, this integral may be divided into three parts.

$$n(\omega) - 1 = \frac{2}{\pi} \int_0^{\omega_l} \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega' + \Delta(\omega) + \frac{2}{\pi} \int_{\omega_h}^\infty \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega'. \quad (5)$$

The first and third terms correspond to dispersion arising from absorptions in the spectral regions from 0 to ω_l , and from ω_h to ∞ , which lie below and above the region of transparency, respectively. Note that these are not principal-value integrals since ω does not lie within the intervals of integration. The second term, written as $\Delta(\omega)$ to emphasize that it is small in the present application, is the principal-value integral representing dispersion arising from the highly transparent region:

$$\Delta(\omega) = \frac{2}{\pi} P \int_{\omega_l}^{\omega_h} \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega'. \quad (6)$$

By assumption $\kappa(\omega)$ is very small for $\omega_l < \omega < \omega_h$, so we neglect $\Delta(\omega)$ in the following. However, if $\kappa(\omega)$ were not negligible, (6) could be evaluated explicitly.

The integrands of the first and third terms on the right-hand side of (5) may be expanded in power series, the first in the variable $(\omega'/\omega)^2$, the third in the variable $(\omega/\omega')^2$. Since the overwhelming contribution to the infrared refractive index of intrinsic semiconductors arises from interband transitions at energies higher than $\hbar\omega_h$, we first consider the third term that accounts for contributions from absorptions above ω_h . Expanding the integrand yields a Taylor series in ω^2

$$\frac{2}{\pi} \int_{\omega_h}^{\infty} \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega' = (n_0 - 1) + n_2\omega^2 + n_4\omega^4 + \dots \quad \omega < \omega_h \quad (7)$$

where

$$n_0 = 1 + \frac{2}{\pi} \int_{\omega_h}^{\infty} \frac{1}{\omega'} \kappa(\omega') d\omega' \quad (8)$$

and

$$n_j = \frac{2}{\pi} \int_{\omega_h}^{\infty} \frac{1}{\omega'^{j+1}} \kappa(\omega') d\omega' \quad j = 2, 4, 6, \dots \quad (9)$$

Provided the absorptions making significant contributions to the integrals in (9) are at frequencies well above the region of transparency, i.e. well above ω_h , the coefficients n_j should fall off rapidly with increasing j so that only a few terms will be required in the series on the right-hand side of (7). (In the event that this condition is not satisfied, the integral can be treated by making a partial expansion and treating the remainder as a separate integral. See (13) below.)

Parenthetically, it should be pointed out that a similar series expansion holds [16] for the molar refractivity of gases in terms of moments of the atomic or molecular dipole oscillator strength. The derivation is based on a quantum-mechanical result for the polarizability and strictly applies to the dielectric function, not the index. Additionally, local-field corrections should be included in the case of dense systems to account for the polarizability of the gas as a whole. The present derivation avoids these complications by explicitly treating n and κ , which refer to the response of the entire solid.

Similarly, contributions to the refractive index from absorptions below ω_l may be written as a series in inverse powers of ω^2 ,

$$\frac{2}{\pi} \int_0^{\omega_l} \frac{\omega'}{\omega'^2 - \omega^2} \kappa(\omega') d\omega' = n_{-2}\omega^{-2} + n_{-4}\omega^{-4} + \dots \quad \omega_l < \omega \quad (10)$$

where

$$n_{-j} = -\frac{2}{\pi} \int_0^{\omega_l} \omega'^{j-1} \kappa(\omega') d\omega' \quad j = 2, 4, 6, \dots \quad (11)$$

Again, provided the region of significant absorption contributing to the integrals in (11) lies at frequencies well below ω_l , convergence of the series (10) should be rapid.

Finally, combining (7) and (10) yields a Laurent expansion [17] for the index

$$n(\omega) = n_0 + \sum_{j=2,4,\dots}^{\infty} n_{-j}\omega^{-j} + n_j\omega^j \quad \omega_l < \omega < \omega_h. \quad (12)$$

From a mathematical standpoint, the moments expressions (8), (9) and (11) for the expansion coefficients are specific instances of the Cauchy–Taylor theorem [17] applied to the complex refractive index. (This theorem relates the coefficients in Taylor and Laurent series to contour integrals in the complex ω plane. Since the index falls off sufficiently rapidly [3] at infinity, just those parts of the integrals along the real axis contribute.) Here, however, only terms in even powers of ω appear in (12) since $n(\omega)$ is an even function of ω in the absence of a magnetic field [15]. Terms in positive powers of ω arise from absorptions above the high-frequency limit of the range of transparency, ω_h , and their coefficients, n_j , are always positive for a system in the ground state (κ is everywhere positive). In contrast, terms in negative powers of ω arise from absorptions below the low-frequency limit, ω_l , and their coefficients, n_{-j} , are always negative for systems in the ground state. We note that the inverse-first-moment expression for the static index, (8), is well known in the limit of $\omega_h \rightarrow 0$ [2]. The remaining expressions for the coefficients, (9) and (11), appear to be new.

Cauchy derived a series representation of the index in this form, but involving only positive powers of ω , on the basis of the ether theory in 1830 [4, 5]. It has received little attention since the development of the electronic theory of matter and the explanation of optical properties in terms of Lorentz oscillators [12] or their quantum counterparts. However, the present dispersion-theory approach shows that a series expansion, when generalized to include negative-power terms, is in principle exact in regions of negligible absorption. Further, the result is general since it depends on the causal, local and linear nature of the optical response of an inertial system. The remaining practical question concerns the number of terms needed to give an adequate representation of the index. To address this we consider the favourable case of nonpolar, indirect-gap semiconductors.

3. Application to elemental semiconductors

Intrinsic elemental semiconductors such as diamond, silicon and germanium are highly transparent for photon energies below the electronic band gap with the exception of a very weak higher-order phonon absorption that is negligible compared with electronic effects [18–20]. (We estimated the phonon contribution to the index to be roughly 10^{-3} or less by approximating the principal infrared absorption bands [21, 22, 25] with Lorentzians and calculating the dispersion. We will neglect this contribution of higher-order phonon processes in the following.) The index of refraction is relatively large throughout this region of transparency—especially so for silicon and germanium—and can be measured directly and with high precision using standard optical techniques. In light of the technological and commercial importance of these materials, a representation of their refractive index that is simple, physically based and appropriate to the precision of the measurements is desirable. The extent to which the first few terms of a Cauchy expansion in positive powers of photon frequency fulfills these criteria is illustrated in figure 1 for high-quality natural diamond [9, 21], and in figure 2 for high-purity silicon [8, 22–24] and germanium [8, 25]. Values of the ‘Cauchy’ coefficients found by fitting these data are given in table 1.

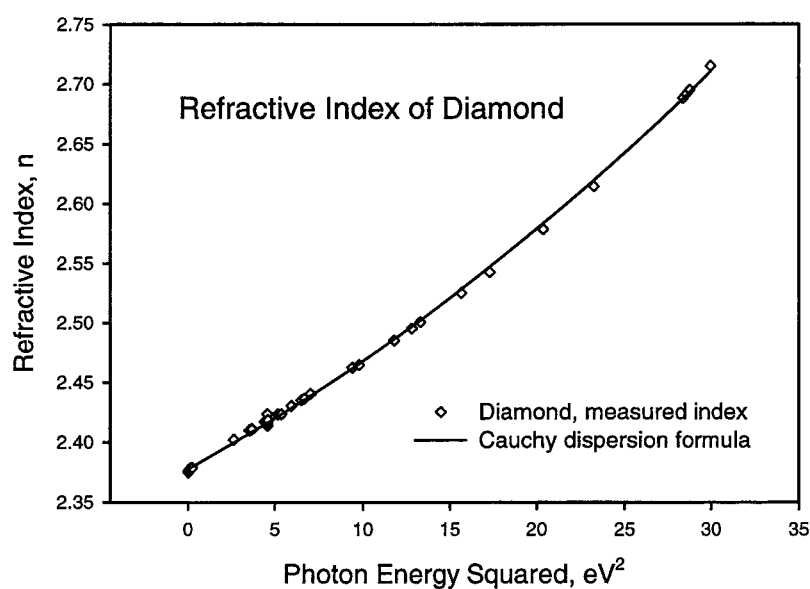


Figure 1. The refractive index of natural diamond as a function of photon energy squared. Data are taken from measurements of Edwards and Ochoa [9] and the compilation of Edwards and Philipp [21].

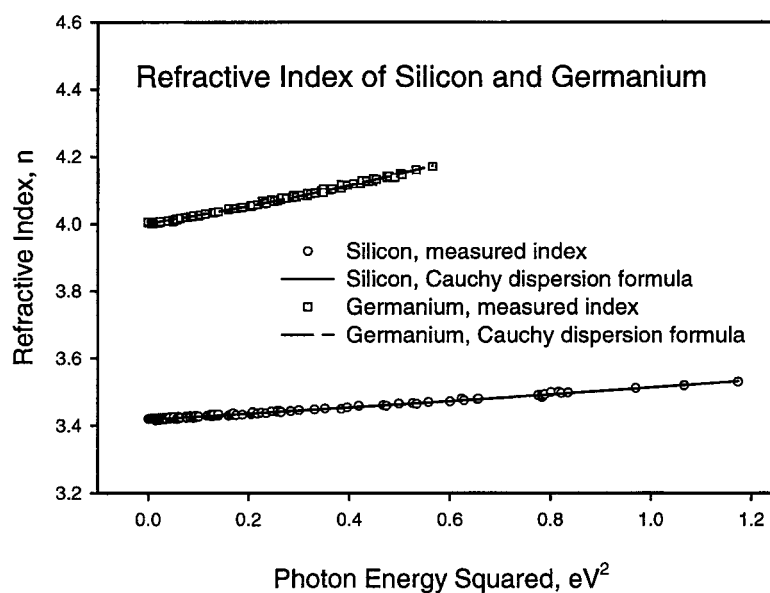


Figure 2. The refractive index of high-purity silicon and germanium in the infrared as a function of photon energy squared. The data are taken from the compilations of Li [8], Edwards [22, 23] and Potter [25]. (In the case of silicon, several early measurements that appear to suffer from systematic errors have not been plotted.)

3.1. Positive-power terms

Over the range of transparencies in which direct measurements are possible—two to two-and-one-half decades in energy—figures 1 and 2 show that the refractive index is very nearly linear in

Table 1. Cauchy expansion coefficients for the refractive index in the range of high transparency of the of group IV semiconductors. Least-squares fits of (12) were made to compilations of direct index measurements given in [9, 21] for diamond, [8, 22–24, 26] for silicon, and [8, 25, 26] for germanium. For intrinsic material n_{-2} should be zero. The small non-zero values are believed to reflect extrinsic absorptions at energies below the range of index measurements. The values of n_{-2} for silicon and germanium given are strongly influenced by the far infrared measurements of Randall and Rawcliffe [26], and hence are specific to the impurities in their samples.

Material	Range (eV)	n_{-2} (eV ²)	n_0	n_2 (eV ⁻²)	n_4 (eV ⁻⁴)
Diamond	0.050–5.47	-1.07×10^{-5}	2.37 ₈	$8.0_1 \times 10^{-3}$	$1.0_4 \times 10^{-4}$
Silicon	0.002–1.08	$-2.0_4 \times 10^{-8}$	3.418 ₉	$8.1_5 \times 10^{-2}$	$1.2_5 \times 10^{-2}$
Germanium	0.002–0.75	-1.0×10^{-8}	4.00 ₃	2.2×10^{-1}	1.4×10^{-1}

ω^2 with a slight upward curvature corresponding to a small ω^4 term with a positive coefficient. The need for only a few terms in the series reflects the gradual onset of relatively weak intrinsic absorption at energies just above the region of transparency in these substances. This is characteristic of nonpolar materials with an indirect-gap electronic structure [19] for which phonon-assisted band-to-band transitions give rise to the low-energy interband excitations. Strong direct interband transitions commonly occur only at significantly higher energies.

Fitting available direct index measurements with a polynomial including terms up to ω^6 does not significantly improve the fit. The resulting values of n_6 are very small and in some instances are negative. A negative coefficient for positive powers of ω is inconsistent with the series-expansion formalism and most likely reflects uncertainties in the published data. (Diamond data were the least well fit, but the fit was still within the range of uncertainty found by Vishnevskii and Malogolovets, who measured a 0.4% variation, or 0.01 uncertainty, in the index amongst 26 samples at 580 nm [27].) We observe, however, that a negative coefficient could arise when index data are fit over a range approaching (as for diamond here) or beyond the onset of indirect transitions. In that event, a more appropriate procedure would be to limit the expansion of the integrand in (9) to the first few term of the series and explicitly retain the remainder as an integral. Thus, an expansion up to terms in ω^4 yields

$$n(\omega) = n_0 + n_2\omega^2 + n_4\omega^4 + \frac{2\omega^6}{\pi} \int_{\omega_h}^{\infty} \frac{\kappa(\omega')}{\omega'^5(\omega'^2 - \omega^2)} d\omega'. \quad (13)$$

For an absorption spectrum consisting of δ -functions at frequencies ω_i , the integral in (13) reduces to a sum of resonance terms somewhat similar to those in the Sellmeier and Herzberger formulae. Moreover, the integral in (13) can take on negative values for ω above the onset of absorptions, and in principle could yield a negative contribution varying as ω^6 to a first approximation. However, for the present materials the onset of absorption is gradual and sufficiently weak that, to within the accuracy of index data examined, there does not appear to be a need for terms in the sixth or higher powers of ω , especially for Si and Ge.

The advantage of the Cauchy representation for the index of nonpolar semiconductors is its simplicity and the connection between expansion coefficients and absorption spectra. This simplicity of $n(\omega)$ – ω^2 plots for silicon and germanium has been recognized previously (see, for example, section 10.4 of [14], and [28]); however, it is rarely exploited.

Aside from the simplicity of the representation, the coefficients found by fitting index measurements provide an independent check on measured absorption spectra. This is useful because the precision of index measurements in the infrared (and the visible in diamond) exceeds that for reflectance or transmittance measurements for photon energies above the band gap by an order of magnitude or more. Consequently, the integral expressions for n_0 , n_2 and n_4 become ‘sum rules’ involving the measured values of the intercept, slope and curvature

of the index that can be used to distinguish between conflicting absorption measurements at higher energies [29].

Table 2. Cauchy expansion coefficients for the refractive index of intrinsic silicon in the infrared as calculated from a fit of (12) to direct index measurements [8, 22–24, 26], and from moments of two proposed composite extinction coefficient spectra calculated with (8) and (9). Uncertainties in the coefficients were estimated by fitting (12) to sets of direct index measurements alternately including and excluding measured points lying significantly above or below the average in the energy range above 0.8 eV.

Source	n_0	n_2 (eV ⁻²)	n_4 (eV ⁻⁴)
Fit to measured $n(\omega)$	3.419 ± 0.005	$8.2 \pm 0.3 \times 10^{-2}$	$1.3 \pm 0.3 \times 10^{-2}$
Shiles and Smith $\kappa(\omega)$ composite [30]	3.39	10.1×10^{-2}	0.77×10^{-2}
Karstens <i>et al</i> $\kappa(\omega)$ composite [6]	3.44	9.1×10^{-2}	0.56×10^{-2}

Table 2 illustrates this with a comparison of Cauchy index coefficients derived from the best fit of a three-term polynomial to the measured index of crystalline silicon, with values of the corresponding integrals calculated from proposed composite absorption spectra for intrinsic silicon [6, 30]. For example, we find that the value of n_0 predicted by the spectra proposed by Shiles and Smith [30] is too low, indicating that this proposed absorption spectrum is shifted toward high energies. Conversely, n_0 calculated from the composite of Karstens *et al* [6] is too large, suggesting a net shift of their proposed absorption spectrum too far toward low energies.

3.2. Negative-power terms

Initially, one would not expect that terms in negative powers of photon frequency would be needed to fit the index data for group IV semiconductors. Intrinsic samples at moderate temperatures should not display significant electronic absorption in the far infrared, and their phonon absorption is negligibly weak. However, on the expanded scale of figures 3 and 4 a significant departure from the near-linear dependence of the index on ω^2 is apparent at low energies. For diamond this occurs below 0.55 eV, and it is strikingly large below 0.03 eV, for silicon. A similar sharp drop occurs in measurements of the index of germanium below 0.01 eV, but the data have more scatter. These drops are inconsistent with a Taylor-series expansion in ω^2 , and indicates that at least one negative-power term is required to accurately reproduce the measurements in all cases. We attribute this anomaly to the ‘tail’ of dispersion associated with extrinsic absorptions at energies below the range of measurements. As we argue below, the extrinsic absorptions in Si and Ge likely arise from free carriers. In diamond, defects or impurity complexes are the likely culprits, since even high-quality natural diamond is known to have impurity contents of the order of a few parts per thousand [31].

A power-series fit to this tail of the low-energy dispersion can provide insight into these low-energy processes. The point is that in general the high-frequency asymptotic form of the dielectric response of matter is [2, 3]

$$\epsilon(\omega) = n(\omega)^2 = 1 - \omega_p^2/\omega^2 \quad \omega \rightarrow \infty \quad (14)$$

where ω_p^2 is the plasma frequency squared, $4\pi Ne^2/m_e$. Here, N is the electron density and e and m_e are the electron charge and mass, respectively. Thus, even if only the high-frequency tail of a dispersion curve is known, the plasma frequency may be estimated. By analogy, one expects that knowledge of the tail of the dispersion associated with absorptions below ω_l , would allow an estimate of their net plasma frequency.

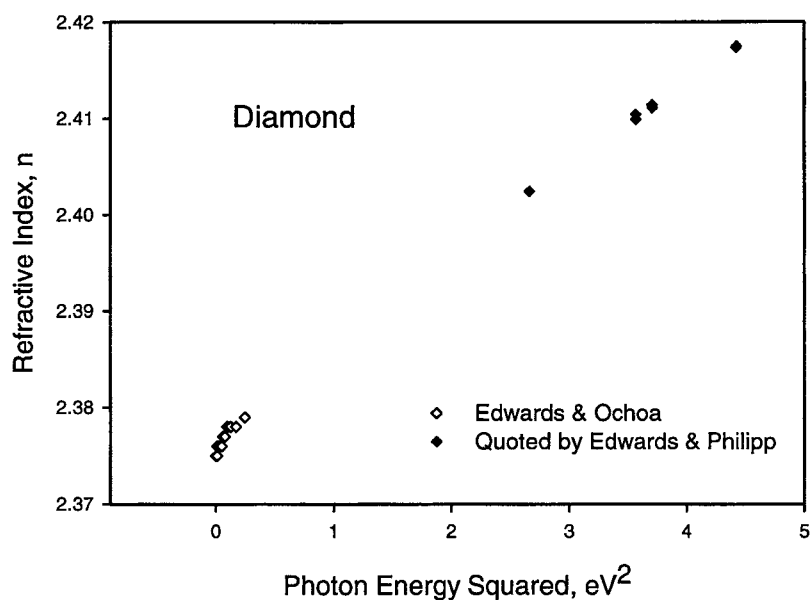


Figure 3. Refractive index of diamond below 2.1 eV [9, 21]. Deviations from the almost linear dependence on ω^2 occur below approximately 0.55 eV and are attributed to polarization associated with ionic absorptions lying at energies below the range of measurements. This polarization is 180° out of phase with the polarization due to band-to-band transitions and, hence, reduces the refractive index.

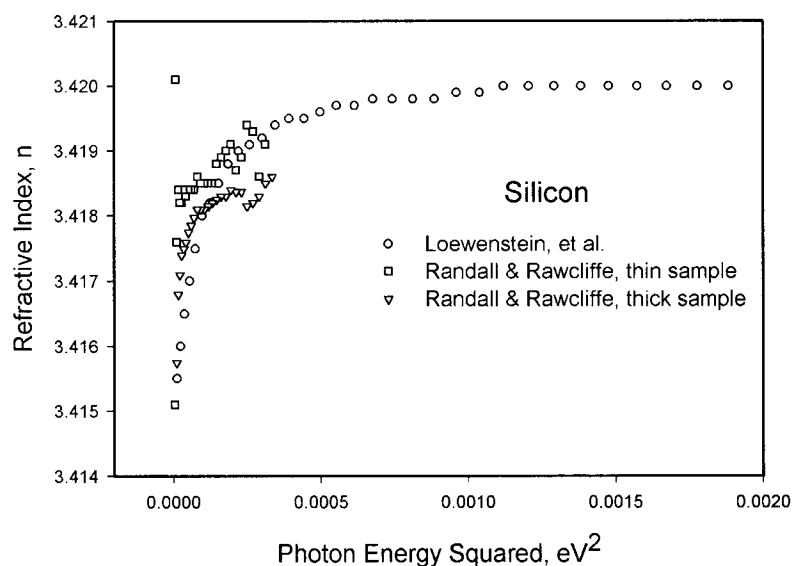


Figure 4. Refractive index of silicon in the far infrared [8, 22, 23]. A sharp decrease is apparent below 0.03 eV in the data of Randall and Rawcliffe [26]; it is attributed to polarization of free carriers.

In making this argument quantitative, we must recognize that the low-energy absorptions should be viewed as taking place in the polarizable medium of the host crystal. Formally this

may be accounted for by writing the dielectric function at the low-energy end of the region of transparency as the superposition of the dielectric response for the high- and low-energy absorptions

$$\epsilon(\omega) = n(\omega)^2 \approx n_0^2 - \Omega_p^2/\omega^2 \quad \omega_l < \omega < \omega_H \quad (15)$$

where Ω_p is the effective plasma frequency associated with the low-energy absorptions. Assuming that the low-energy dispersion, i.e. the second term in (15), is small compared with n_0 , the index becomes

$$n(\omega) \approx n_0 - \frac{1}{2n_0} \Omega_p^2/\omega^2 \quad (16)$$

and we can identify the coefficient n_{-2} in the Laurent series as

$$n_{-2} = -\frac{\Omega_p^2}{2n_0}. \quad (17)$$

In a single-oscillator model for the low-energy absorption, Ω_p^2 becomes $4\pi Nq^2/m_{eff}$, where N is the density of the low-frequency oscillators, q is their effective charge and m_{eff} their effective mass. Values of the plasma frequency for the low-frequency absorption inferred from fits of the polynomial $n_{-2}\omega^{-2} + n_0 + n_2\omega^2 + n_4\omega^4$ to refractive-index measurements are given in table 3. In all cases, and especially for the Si and Ge samples, the plasma frequency is small, which is consistent with low impurity content and/or high effective mass.

Table 3. The plasma frequency, Ω_p , for extrinsic far-infrared polarization in elemental semiconductor samples determined from the ω^{-2} component of the generalized Cauchy dispersion formula as fit to measurements of the refractive index. The ratio of the atomic fraction of defects in the sample, φ , to their effective mass ratio, μ , has been calculated from the plasma frequency using the material-dependent constant given in the third column (see text for details). The probable process responsible for the low-energy polarization has been inferred from the φ/μ ratio and the reported sample purity.

Material	$\hbar\Omega_p$ (eV)	$4\pi e^2/m_e$ (eV ²)	φ/μ (per atom)	Process
Diamond, natural	7.1×10^{-3}	243.1	2.1×10^{-7}	Ionic
Silicon	3.7×10^{-4}	68.90	2.0×10^{-9}	Electronic
Germanium	2.8×10^{-4}	60.93	1.3×10^{-9}	Electronic

To estimate the density of extrinsic oscillators, we write their spacial density, N , as $\varphi\rho$, where ρ is the atomic density of the solid and φ the fraction of defects or impurities per host crystal atom. Further, we assume the oscillators' effective charge, q , is approximately the electronic charge, e , and we measure the effective mass in units of the electronic mass as $\mu = m_{eff}/m_e$. Then the plasma frequency can be written as

$$\Omega_p^2 = \frac{4\pi Nq^2}{m_{eff}} = \left\{ \frac{4\pi\rho e^2}{m_e} \right\} \frac{\varphi}{\mu}. \quad (18)$$

The term in curly brackets on the right-hand side of (18) may be evaluated from the known crystal structure [32] and the ratio φ/μ then calculated from the observed values of Ω_p . The results are summarized in table 3. For all three group IV elements φ/μ is very small, corresponding to either a small fraction of impurities or defects, or a large effective mass.

In natural diamond, nitrogen is known to be present at levels of parts per thousand. Additionally, hydrogen, boron and many other impurities are present in smaller amounts [31]. Assuming impurity and/or lattice-defect concentrations of the order of $\varphi \approx 10^{-3}$, the observed value of $\varphi/\mu \approx 10^{-7}$ is consistent with effective mass of the order of $10^4 m_e$, that is, an

ionic mass. We therefore conclude that the principal contributor to the extrinsic far-infrared dispersion in natural diamond is the polarization of either charged lattice defects or ionic impurities. Since a variety of defects, as well as some free-carrier absorption, are expected in natural diamond [31], the present analysis provides only modest insight into low-energy optical processes. However, the value of Ω_p found and the observed drop in $n(\omega)$ below ≈ 550 meV are consistent with a picture of polar-lattice defects that couple the electromagnetic field to local phonon modes or lattice phonons, which in diamond have energies from 0 to 165 meV, with a strong density-of-states peak at 150 meV [33].

The silicon and germanium samples studied in the far infrared were reportedly of high purity, with resistivities greater than $10 \Omega \text{ cm}$ [26]. From the observed relation between resistivity and dopant levels [34], this corresponds to impurity concentrations between 10^{14} and 10^{15} cm^{-3} . The ratio, ϕ , of impurity concentration to host-crystal atomic density [32] is then of the order of 10^{-8} to 10^{-9} . Comparing this with the ratio $\phi/\mu \approx 10^{-9}$ (table 3, column 4) derived from fits to the index, leads to effective masses of the order of the electron mass. Thus, we conclude that the extrinsic polarization in these Si and Ge samples arises from electronic processes, presumably free-carrier absorption. Since the effective masses of electrons and holes are of the same order of magnitude [35], the available data do not allow us to distinguish the carrier type.

This conclusion is strengthened by considering the phonon modes in Si and Ge. In the former, lattice modes extend to energies of 65 meV with a density-of-states peak at 62 meV, whilst for the latter they extend to 38 meV with the maximum in the density of states at 36 meV. In both index data sets considered here, index measurements extended down to ≈ 2 meV with the sharp drop in index starting at ≈ 30 meV for silicon and ≈ 10 meV for germanium. There is, however, little or no evidence of structure in the region of high phonon density of states, which would be expected if there were a significant number of polar lattice defects which coupled phonon modes to the photon field.

4. Summary

We have derived a generalization of Cauchy's power-series expansion for the refractive index of an insulator or semiconductor in its range of transparency. The expansion coefficients are shown to be the odd moments of the absorption spectra above and below the transparent range. The formalism is illustrated using literature values for the infrared refractive index for high-purity silicon and germanium and for the infrared and visible index of high-quality diamond. We find that for intrinsic material a series up to terms in ω^4 is sufficient to fit the measurements to within present experimental uncertainty. However, even high-purity samples display extrinsic effects arising from free carriers, impurities or defects in the far infrared. The contributions of these extrinsic absorptions to the refractive index can be adequately represented by a single term in ω^{-2} . The coefficient of this term may be related to the average plasma frequency of the extrinsic absorption by comparison of the index with the high-frequency response of an oscillator embedded in a dielectric, and the concentration of extrinsic absorbers then estimated from the plasma frequency.

Acknowledgments

The authors would like to acknowledge insightful discussions with Dr Joseph Berkowitz, the assistance of Messrs Gary Davidoff and Angus Robertson of the ANL and UVM libraries, and the hospitality of the Physics Division of Argonne National Laboratory during the course of

this research. Work at Argonne was supported by the US Department of Energy, Office of Science, Nuclear Physics Division, under contract No W-31-109-Eng-38.

References

- [1] Kubo R, Toda M and Hashitsume N 1991 *Statistical Physics* vol 2 (Berlin: Springer) especially chapters 3 and 4
- [2] Stern F 1963 *Solid State Physics* vol 15, ed F Seitz and D Turnbull (New York: Academic) pp 299–408
- [3] Altarelli M, Dexter D L, Nussenzveig H M and Smith D Y 1972 *Phys. Rev. B* **6** 4502–9
- [4] Cauchy A L 1830 *Bull. Sci. Math.* **14** 6–10 (especially 9)
- [5] Cauchy A L 1836 *Mémoire sur la Dispersion de la Lumière* (Prague: Calve)
- [6] Karstens W, Smith D Y and Inokuti M 2000 *Bull. Am. Phys. Soc.* **45** 742
- [7] Shiles E, Sasaki T, Inokuti M and Smith D Y 1980 *Phys. Rev. B* **22** 1612–28
- [8] Li H H 1980 *J. Phys. Chem. Ref. Data* **9** 561–658. Note: tabulated n values attributed to Cardona *et al* and to Randall *et al* in this reference appear to have been incorrectly read from graphs. Corrected values have been used in the present study.
- [9] Edwards D F and Ochoa E 1981 *J. Opt. Soc. Am.* **71** 607–8
- [10] For a brief history of the Sellmeier and other dispersion formulae, see Wolf K L and Herzfeld K F 1928 *Handbuch der Physik* ed H Geiger and K Scheel, vol 20 (Berlin: Springer) ch 10
- [11] Herzberger M 1959 *Opt. Acta* **6** 197–215
- [12] Lorentz H A 1909 *The Theory of Electrons* (Leipzig: Teubner)
- [13] Kramers H A 1928 *Atti Congr. Int. Fisici (Como–Pavia–Roma)* vol 2 (Bologna: Zanichelli) pp 545–57
- [14] Kronig R de L 1926 *J. Opt. Soc. Am.* **12** 547–57
- [15] Moss T S 1959 *Optical Properties of Semi-Conductors* (London: Butterworths)
- [16] Smith D Y 1976 *J. Opt. Soc. Am.* **66** 454–60
- [17] Fano U and Cooper J S 1968 *Rev. Mod. Phys.* **40** 441–507
- [18] Titchmarsh E C 1939 *The Theory of Functions* 2nd edn (Oxford: Oxford University Press)
- [19] Greenaway D L and Harbeke G 1968 *Optical Properties and Band Structure of Semiconductors* (Oxford: Pergamon)
- [20] Cohen M L and Chelikowsky J R 1988 *Electronic Structure and Optical Properties of Semiconductors* (Berlin: Springer)
- [21] For electronic and optical data see, *Landolt-Börnstein New Series* 1982 vol 17a, ed O Madelung, M Schulz and H Weiss (Berlin: Springer) 36–127
- [22] Edwards D E and Philipp H R 1985 *Handbook of Optical Constants of Solids* vol 1, ed E D Palik (New York: Academic) pp 665–73
- [23] Edwards D F 1985 *Handbook of Optical Constants of Solids* vol 1, ed E D Palik (New York: Academic) pp 547–69
- [24] Edwards D F 1988 *Handbook of Optical Constants of Solids* vol 3, ed E D Palik (New York: Academic) pp 531–6
- [25] Aspenes D E 1988 *Properties of Silicon* (London: INSPEC) pp 61–79
- [26] Potter R F 1985 *Handbook of Optical Constants of Solids* vol 1, ed H D Palik (New York: Academic) pp 465–78
- [27] Randall C M and Rawcliffe R D 1967 *Appl. Opt.* **6** 1889–95
- [28] Vishnevskii A S and Malogolovets V G 1973 *Dopov. Akad. Nauk Ukr. RSR A* **35** 892–95
- [29] Primak W 1971 *Appl. Opt.* **10** 759–63
- [30] Smith D Y, Inokuti M and Karstens W 2000 *Phys. Essays* **13** at press
- [31] Shiles E J and Smith D Y 1978 *Bull. Am. Phys. Soc.* **23** 226
- [32] Davies G 1984 *Diamond* (Bristol: Hilger)
- [33] Donohue J 1974 *The Structure of the Elements* (New York: Wiley)
- [34] Bilz H and Kress W 1979 *Phonon Dispersion Relations in Insulators* (Berlin: Springer) pp 95–8
- [35] Irvin J C 1962 *Bell Syst. Tech. J.* **41** 387–410
- [36] Kittel C 1996 *Introduction to Solid State Physics* 7th edn (New York: Wiley) pp 214–16