

Optical Properties of Semiconductors

H. R. PHILIPP AND H. EHRENREICH

General Electric Research Laboratory, Schenectady, New York

(Received 17 September 1962)

Reflectance data are presented for Si, Ge, GaP, GaAs, InAs, and InSb in the range of photon energies between 1.5 and 25 eV. The real and imaginary parts of the dielectric constant and the function describing the energy loss of fast electrons traversing the materials are deduced from the Kramers-Kronig relations. The results can be described in terms of interband transitions and plasma oscillations. A theory based on the frequency-dependent dielectric constant in the random phase approximation is presented and used to analyze these data above 12 eV, where the oscillator strengths coupling the valence and conduction bands are practically exhausted. The theory predicts and the experiments confirm essentially free electron-like behavior before the onset of d -band excitations and a plasma frequency modified from that of free electrons due to oscillator strength coupling between valence and d bands and d -band screening effects. These complications are absent in Si. The energy loss functions obtained from optical and characteristic energy loss experiments are also found to be in good agreement. Arguments for interpreting structure in the reflectance curves above 16 eV in terms of d -band excitations are given.

1. INTRODUCTION

THE optical properties of solids may be determined by Kramers-Kronig analysis of normal incidence reflectance data.¹⁻³ This procedure evaluates the real and imaginary parts of the dielectric constant which describe these properties. The curves shown in Fig. 1 for InSb are typical of the results for semiconductors.

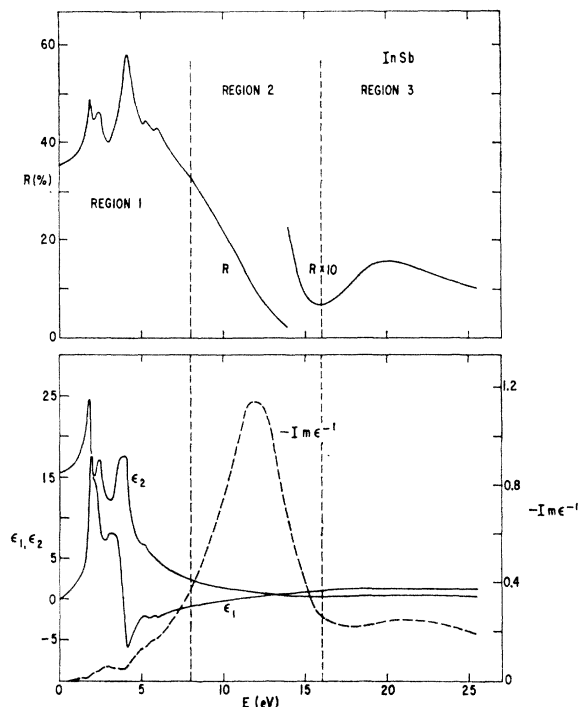


FIG. 1. The spectral dependence of the reflectance R , the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy loss function $-\text{Im}\epsilon^{-1}$ for InSb.

Three spectral regions are distinguished.⁴ The first region extending to about 8 to 10 eV is characterized by sharp structure associated with valence to conduction band transitions.⁵ The second region, which extends to about 16 eV, is marked by a rapid decrease of the reflectance which is reminiscent of the behavior of certain metals in the ultraviolet.^{4,6} Here one may think of the valence electrons as essentially unbound and able to perform collective oscillations. In the third region, the reflectance again rises indicating the onset of additional optical absorption. This structure is associated with transitions between filled d bands, lying below the valence band, and empty conduction band states.^{4,7}

The function $-\text{Im}\epsilon^{-1}$, describing the energy loss of fast electrons traversing the material,⁸ is also shown in Fig. 1. Sharp maxima in this function have been frequently associated with the existence of plasma oscillations.⁹ A maximum of this type is seen to occur in region 2.

It is the purpose of this paper to present an account of the physics to be learned from optical studies on semiconductors. The interpretation of data in the first region has already been given in reference 5. This paper is concerned mainly with the remaining two regions. Curves similar to Fig. 1 for Si, Ge, GaAs, GaP, and InAs are presented in Sec. 2 together with a discussion of the experimental procedure. The theoretical framework for interpreting these data is outlined in Sec. 3. The interpretation of the experimental results is discussed in Sec. 4.

⁴ H. Ehrenreich and H. R. Philipp, International Conference on Semiconductor Physics, Exeter, July, 1962 (to be published).

⁵ H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).

⁶ H. Ehrenreich and H. R. Philipp, Bull. Am. Phys. Soc. **7**, 78 (1962).

⁷ H. R. Philipp and H. Ehrenreich, Phys. Rev. Letters **8**, 1 (1962).

⁸ See, for example, P. Nozières and D. Pines, Phys. Rev. **113**, 1254 (1959).

⁹ L. Marton, Rev. Mod. Phys. **28**, 172 (1956).

¹ F. C. Jahoda, Phys. Rev. **107**, 1261 (1957).

² H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959); **120**, 37 (1960); **127**, 159 (1962).

³ H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

2. EXPERIMENTAL

Measurements of reflectance were obtained in the range 1.5 to 25 eV using a vacuum grating monochromator similar in design to that of Johnson.¹⁰ This instrument is shown schematically in Fig. 2(a). Light from a tungsten bulb or discharge lamp is incident on a concave grating near normal incidence. The grating is rotated about an off-axis pivot which, in effect, moves the grating-to-slit distance more in accord with a Rowland mount while still retaining the advantages of simplicity, compactness, and constant angle of emergence at the exit slit.¹¹ The sample chamber is vacuum sealed to the monochromator. Specimens are mounted on each of the four sides of the sample holder which is rotated into position for measurement of the reflected intensity. The holder is pulled down out of the beam for measurement of incident intensity. For wavelengths in the vacuum ultraviolet, the photomultiplier detectors are coated with sodium salicylate phosphor.

The discharge lamp used for most of the spectral range is shown schematically in Fig. 2(b). The main feature is the use of a quartz capillary to concentrate the arc and to effect an increased voltage drop. Typical operating conditions are given in the figure.

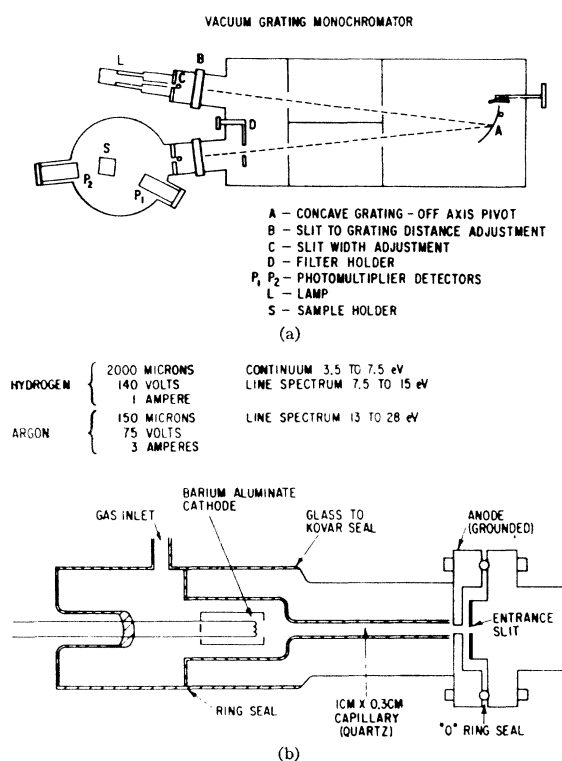


FIG. 2. Schematic drawing of the experimental apparatus. (a) Monochromator and sample chamber; (b) light source.

¹⁰ P. D. Johnson, *J. Opt. Soc. Am.* **42**, 278 (1952).

¹¹ P. D. Johnson, *Rev. Sci. Instr.* **28**, 833 (1957).

The spectral dependence of the reflectance for Si, Ge, InAs, GaAs, and GaP is shown in Fig. 3.¹² Below 1.5 eV, the curves are extrapolated to values computed from dielectric constant measurements.¹³ In the case of the 3-5 compounds, the data represent measurements obtained on one sample of each material.

Samples were etched to remove chemical layers such as oxides and distorted layers produced by mechanical polishing. After etching the specimens were exposed to air for the minimum of time necessary for mounting in the sample chamber and then, for a longer time, to the poor vacuum of the monochromator during measurement. The samples are conceivably subject to atmospheric contamination and the data should be treated with some caution until further studies, admittedly more difficult, can be made on bulk surfaces prepared under conditions of ultrahigh vacuum. We consider the results adequate for the physical interpretation to be discussed in this paper.

The dielectric constants, as well as the energy loss function, obtained from Kramers-Kronig analysis are also shown in Fig. 3.

3. COMPLEX DIELECTRIC CONSTANT FOR AN INSULATOR

The complex frequency-dependent dielectric constant is very useful in the description of the optical properties of a system.^{8,14} In the limit of long wavelengths, which is the one of interest in discussions of ordinary optical properties, and for cubic materials, the dielectric constant tensor is a scalar.¹⁵ Thus, the response of electrons in the system to either transverse or longitudinal disturbances (e.g., photons or fast electrons) may be described in terms of the same quantity. In the random phase approximation (RPA), in particular, the equality of the transverse and longitudinal dielectric constants under these conditions follows in a straightforward manner.¹⁵ This result implies that once the real and imaginary parts of the dielectric constant are accurately known from optical data, some of the results of characteristic energy loss experiments can be inferred.

An explicit expression for the complex dielectric constant of an insulator, valid in the random phase approximation, and generalized to include damping effects in a qualitative sense, may be obtained from the

¹² For other reflectance measurements in the vacuum ultraviolet see T. Sasaki and K. Ishiguro, *Phys. Rev.* **127**, 1091 (1962); O. P. Rustgi, J. S. Nodvik, and G. L. Weissler, *ibid.* **122**, 1131 (1961).

¹³ C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon Press, New York, 1961); M. Hass and B. W. Henvis, *J. Phys. Chem. Solids* **23**, 1099 (1962).

¹⁴ H. Fröhlich and H. Pelzer, *Proc. Phys. Soc. (London)* **A68**, 525 (1955).

¹⁵ S. L. Adler, *Phys. Rev.* **126**, 413 (1962).

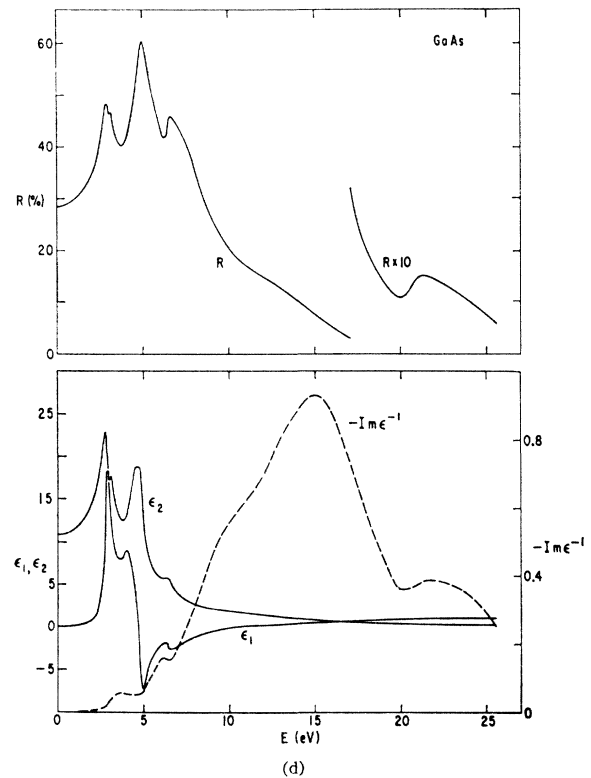
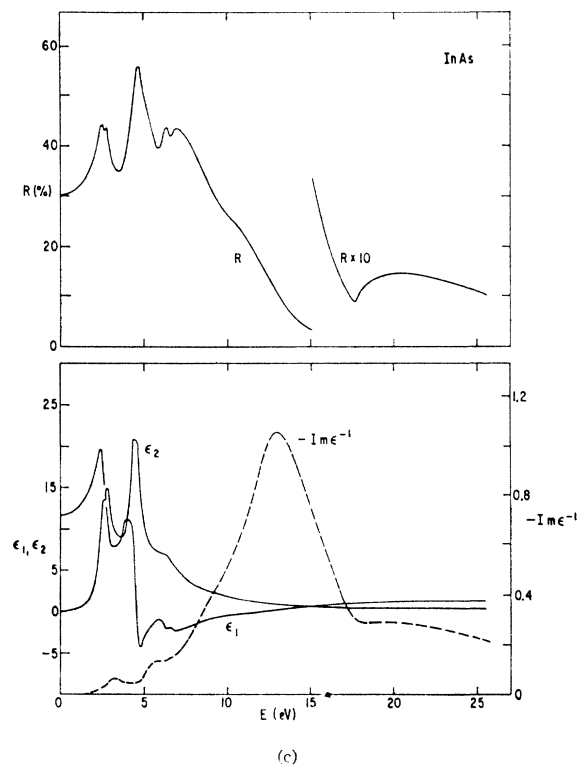
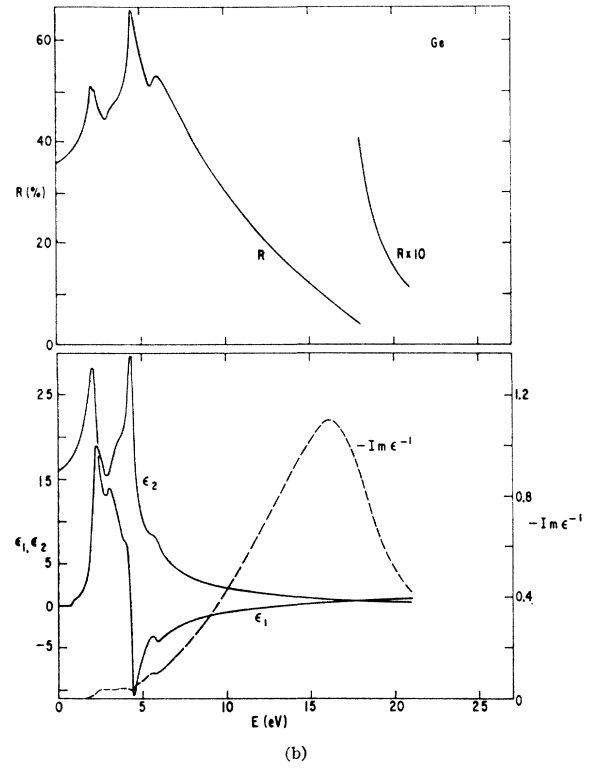
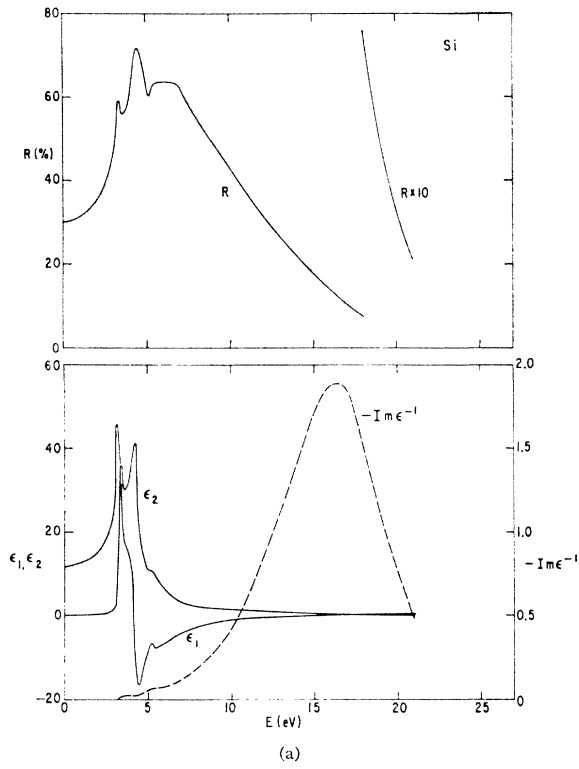
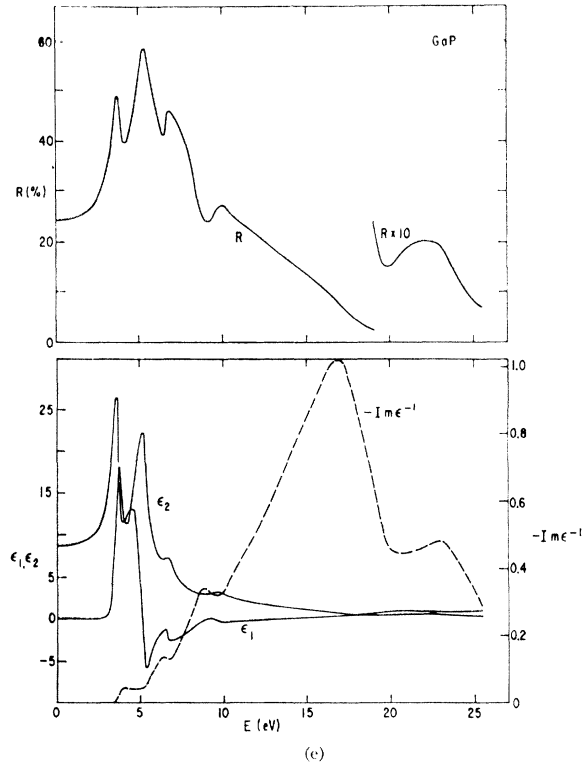


FIG. 3. The spectral dependence of the reflectance R , the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy loss function $-\text{Im}\epsilon^{-1}$ for Si, Ge, InAs, GaAs, and GaP.



results of Ehrenreich and Cohen.¹⁶ We find

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

where $f_l(k)$ is the Fermi distribution,

$$f_{ll'} = (2/\hbar\omega_{ll'}) |P_{ll'}|^2$$

is the momentum matrix element (in the notation of reference 16) of the component p^μ along the direction of propagation, and $\hbar\omega_{ll'} = E_{l'}(k) - E_l(k)$, $E_l(k)$ being the energy of an electron having wave number k in band l . The damping effects, described by a relaxation time $\tau_{ll'}$, which is assumed to depend on the band indices l and l' , are incorporated essentially by replacing the frequency ω by the complex frequency $\omega + i/\tau_{ll'}$, or more precisely, in the manner indicated by footnote 19 of reference 3. For the photon energies of interest here a semiconductor may be considered to be an insulator to good approximation, since the number of carriers produced by intrinsic excitation or doping is generally sufficiently small so that it has negligible effect on the optical properties. Because $f_l(k) = 0$ or 1 for unfilled or filled bands, $f_{l'l} = -f_{ll'}$, and the denominator in (1)

¹⁶ H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

is symmetrical in l and l' , it can be shown that the summation can be written in either of the following forms:

$$\sum_{ll'} = \sum_{l \leq l'} = \sum_{l \leq l', l' > l}$$

where L is the uppermost filled valence band.

It is of interest to exhibit some special forms of Eq. (1) which are particularly useful in connection with the interpretation of the optical properties of semiconductors in the vacuum ultraviolet.

Single Group of Valence Bands

For a semiconductor like Si having a single group of valence bands v which are energetically well isolated from the core states, Eq. (1) reduces to a particularly simple form in the region where the photon frequency ω is larger than ω_{fv} , a typical frequency at which the f -sum rule,

$$\sum_l f_{lv} = 1 - (m/\hbar^2) \partial^2 E_v(k) / \partial k_\mu^2, \quad (2)$$

is exhausted. The frequency ω_{fv} corresponds roughly to that separating regions 1 and 2 in Fig. 1, since the exhaustion of the f -sum rule should be marked experimentally by the absence of further sharp structure due to interband transitions originating from the valence bands. If it is assumed further that core states do not contribute in the frequency range in question (in Si, they lie about 80 eV below the valence bands¹⁷) then

¹⁷ J. C. Phillips and L. Kleinman, quoted by L. Liu, Phys. Rev. **126**, 1317 (1962).

Eq. (1) becomes

$$\epsilon(\omega) \sim 1 - m^{-1} \left(\frac{e}{\pi} \right)^2 \sum'_{v,l} (\omega + i\tau_{vl}^{-1})^{-2} \int d^3k f_{lv}{}^\mu. \quad (3)$$

In order to make further progress, it is necessary to assume that $\tau_{vl} = \tau_v$ depends only on the valence-band index v . Then use of the f -sum rule given by Eq. (2) yields

$$\sum'_{v,l} \int d^3k f_{lv}{}^\mu = \sum_v \int_{\text{BZ}} d^3k = 4\pi^3 \sum_v n_v,$$

where n_v is the particle density in a filled valence band v and the integral extends over the Brillouin zone. The asymptotic result obtained is then

$$\epsilon(\omega) \sim 1 - \omega_{Pv}{}^2 (\omega + i/\tau_v)^{-2}, \quad (4)$$

which, except for its dependence on τ_v , has the same form as the Drude formula. It is to be emphasized that Eq. (4) involves the *free* electron plasma frequency $\omega_{Pv}{}^2 = 4\pi e^2 \sum_v n_v/m$ of the valence bands. The behavior of the valence electrons is, therefore, like that of unbound particles.

Two Separated Groups of Filled Bands

The semiconductors of interest in this category are those like Ge and InSb, having both valence and d bands and for which the lowest excitation frequency of the d bands into conduction band states ω_{cd} is greater than ω_{fv} . Again, the frequency range of interest is $\omega > \omega_{fv}$, that is, the range corresponding to regions 2 and 3. It is clear from the f -sum rule that the d bands can affect the optical properties already in region 2, before real transitions between the d and conduction bands are energetically possible. If there exists an appreciable oscillator strength coupling f_{dv} between the valence and d bands, then this coupling will make a negative contribution to the f -sum and, therefore, cause an enhancement of the oscillator strengths f_{cv} connecting the valence and conduction bands, averaged over the Brillouin zone.

This becomes clearer from an examination of Eq. (1) whose real and imaginary parts are

$$\begin{aligned} \epsilon_1(\omega) &= 1 - (\omega^2 - \tau_v^{-2})(\omega^2 + \tau_v^{-2})^{-2} \\ &\quad \times \left[\omega_{Pv}{}^2 + m^{-1} \left(\frac{e}{\pi} \right)^2 \int d^3k f_{vd} \right] \\ &\quad - m^{-1} \left(\frac{e}{\pi} \right)^2 \int d^3k \sum_{l>v} f_{ld}{}^\mu g_{ld}{}^R, \\ \epsilon_2(\omega) &= \left(\frac{2\omega}{\tau_v} \right) (\omega^2 + \tau_v^{-2})^2 \left[\omega_{Pv}{}^2 + m^{-1} \left(\frac{e}{\pi} \right)^2 \int d^3k f_{vd} \right] \\ &\quad - m^{-1} \left(\frac{e}{\pi} \right)^2 \int d^3k \sum_{l>v} f_{ld}{}^\mu g_{ld}{}^I, \end{aligned} \quad (5)$$

where $g_{ld}{}^R$ and $g_{ld}{}^I$ are, respectively, the real and imaginary parts of

$$g_{ld} = (\omega - \omega_{ld} + i/\tau_{ld})^{-1} (\omega + \omega_{ld} + i/\tau_{ld})^{-1},$$

ω_{Pv} is the plasma frequency of the valence electrons, and τ_v and τ_d are relaxation times associated, respectively, with the valence and d electrons. The term involving f_{vd} arises because the valence-band oscillator strength must be completed before the asymptotic form given in Eq. (4) can be used. Equation (5) consists of a linear superposition of a term due to the valence electrons which are essentially unbound in this frequency range, and one due to the bound d electrons. The term involving $g_{ld}{}^R$ makes a positive contribution to ϵ_1 . It will be shown presently that for $\omega \ll \omega_{ld}$ it corresponds just to the contribution $\delta\epsilon_0$ of the d electrons to the optical dielectric constant above the reststrahlen frequency. The term involving $g_{ld}{}^I$ makes a positive contribution to ϵ_2 . It describes real transitions between the d band and empty conduction band states and will be small until such transitions become energetically allowed. For the frequency range $\omega_{fv} < \omega < \omega_{cd}$, the complex dielectric constant may, therefore, be written approximately in the form

$$\epsilon(\omega) = (1 + \delta\epsilon_0) [1 - \Omega_{Pv}{}^2 / (\omega + i/\tau_v)^2], \quad (6)$$

where

$$\begin{aligned} \Omega_{Pv} &= \left[\omega_{Pv}{}^2 + m^{-1} \left(\frac{e}{\pi} \right)^2 \int d^3k f_{vd}{}^\mu \right] / (1 + \delta\epsilon_0)^{1/2} \\ &\equiv - \frac{\Omega_{Pv}'}{(1 + \delta\epsilon_0)^{1/2}} \end{aligned} \quad (7)$$

is an effective plasma frequency which is enhanced over the free-electron value by a term involving the coupling between the v and d electrons, and diminished by the screening effect due to the d band. Equation (6) closely resembles the Drude-like formula given by Eq. (4). In fact, if the d bands are sufficiently far removed and uncoupled from the valence bands, Eq. (4) is recovered. When the frequency approaches ω_{cd} , the frequency dependence of the last term in the two Eqs. (5) should really be taken into account. This dependence, however, will be seen to be weak, and the present treatment for the sake of simplicity will assume that $\delta\epsilon_0$ in Eq. (6) is real and constant.

For much larger frequencies, when the f -sum rule for the d band is also exhausted, Eq. (1) again assumes a simple asymptotic form:

$$\epsilon(\omega) = \epsilon_0 - \omega_{Pv}{}^2 / (\omega + i/\tau_v)^2 - \omega_{Pd}{}^2 / (\omega + i/\tau_d)^2. \quad (8)$$

The plasma frequency then is given by $\omega_P{}^2 = \omega_{Pv}{}^2 + \omega_{Pd}{}^2$, and corresponds to the total density $n_v + n_d$ of v and d electrons.

Sum Rules

In order to permit comparison of Eq. (6) with the experimental results in region 2, it is desirable to obtain estimates of Ω_{Pv} and $\delta\epsilon_0$. Several sum rules involving the imaginary part of the dielectric constant are useful in this as well as other connections. The first of these,

$$\epsilon_0 = 1 + \left(\frac{2}{\pi}\right) \int_0^\infty \omega^{-1} \epsilon_2(\omega) d\omega, \quad (9)$$

is an expression for the static or optical dielectric constant (below or above the reststrahlen frequency) which is obtained as an elementary consequence of the Kramers-Kronig relations.⁸ The static dielectric constant results if the infrared lattice absorption is taken into account in the integration, and the optical dielectric constant is obtained otherwise. This equation has been previously applied with good success by Philipp and Taft to optical data on Ge and Si.²

The sum rules

$$\int_0^\infty \omega \epsilon_2(\omega) d\omega = \frac{1}{2} \pi \omega_P^2, \quad (10)$$

$$\int_0^\infty \omega \text{Im} \epsilon^{-1}(\omega) d\omega = -\frac{1}{2} \pi \omega_P^2, \quad (11)$$

where ω_P is the free-electron plasma frequency corresponding to the *total* electron density of the system, are also completely general and valid for an arbitrary many-electron system.⁸

It will prove useful to rewrite Eqs. (9) and (10) for finite intervals of integration, and to present explicit expressions for the integrals using the RPA results for ϵ_2 .

Since, in the absence of d bands, the result given by Eq. (10) for an infinite range of integration would involve a plasma frequency characteristic simply of four electrons per atom each having the free-electron mass, it is simplest to express the results of the integration over a finite range 0 to ω_0 in terms of n_{eff} , an effective number of free electrons contributing to the optical properties in this range:

$$\left(\frac{2\pi^2 N e^2}{m}\right) n_{\text{eff}} = \int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega. \quad (12)$$

Here N is the atom density of the crystal. Similarly, the effective dielectric constant, $\epsilon_{0,\text{eff}}$, produced by interband transitions in this range may be written

$$\epsilon_{0,\text{eff}} = 1 + \left(\frac{2}{\pi}\right) \int_0^{\omega_0} \omega^{-1} \epsilon_2(\omega) d\omega. \quad (13)$$

Direct integration, using ϵ_2 as obtained from Eq. (1)

then yields:

$$\left(\frac{2\pi^2 N e^2}{m}\right) n_{\text{eff}} = (2m)^{-1} \left(\frac{e}{\pi}\right)^2 \int d^3k \sum f_{\nu l^\mu} h_{\nu l^-}(\omega_0), \quad (14)$$

$$\epsilon_{0,\text{eff}} = 1 + (\pi m)^{-1} \left(\frac{e}{\pi}\right)^2 \int d^3k \times \sum f_{\nu l^\mu} (\omega_{\nu l}^2 + \tau_{\nu l}^{-2}) h_{\nu l^+}(\omega_0), \quad (15)$$

where

$$h_{\nu l^\pm}(\omega_0) = \tan^{-1}(\omega_0 - \omega_{\nu l}) \tau_{\nu l} + \tan^{-1}(\omega_0 + \omega_{\nu l}) \tau_{\nu l} \pm (2\omega_{\nu l} \tau_{\nu l})^{-1} \ln \frac{(\omega_0 + \omega_{\nu l})^2 + \tau_{\nu l}^{-2}}{(\omega_0 - \omega_{\nu l})^2 + \tau_{\nu l}^{-2}} \quad (16)$$

and $\tau_{\nu l}$ has been assumed independent of frequency. The summation may be taken in the same forms as in Eq. (1). This follows from the fact that $h_{\nu l^\pm}(\omega_0)$ is symmetrical in the indices l and l' . It is seen from Eq. (16) that in the limit $|\omega_{\nu l}| \tau_{\nu l} \rightarrow \infty$, $h_{\nu l^\pm}$ is a step function: $h_{\nu l^\pm} = 0$ for $\omega_0 < \omega_{\nu l}$ and $h_{\nu l^\pm} = \pi$ for $\omega_0 > \omega_{\nu l}$. As $\tau_{\nu l}$ decreases the step is smeared out, principally in the direction of higher energies for $h_{\nu l^-}$, and towards lower energies for $h_{\nu l^+}$. However, $h_{\nu l}(\infty) = \pi$ independently of $\tau_{\nu l}$. Thus, for $\omega_0 \rightarrow \infty$, our results reduce to the exact ones given by Eqs. (9) and (10).

The step-like character of $h_{\nu l}$ results from the fact that ϵ_2 describes real optical transitions and that ω_0 must be such that they are energetically allowed. Thus, there will be a fairly rapid increase in both n_{eff} and $\epsilon_{0,\text{eff}}$ as ω_0 passes across a strong absorption edge. From plots of $\epsilon_{0,\text{eff}}$ vs $\hbar\omega_0$, for example, it is, therefore, possible to estimate which transitions make the most important contribution to the static dielectric constant. More important for the present purposes is the fact demonstrated in the following section, that the quantities Ω_{Pv} and $\delta\epsilon_0$ may also be estimated from such plots.

In this connection it is useful to examine Eqs. (14) and (15) for the case of two sets of filled bands v and d as treated in the preceding subsection. The frequency range of interest is, again, $\omega_0 > \omega_{fv}$. We find in this case

$$\int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega = \frac{1}{2} \pi \Omega_{Pv}^2 + (\pi m)^{-1} \left(\frac{e}{\pi}\right)^2 \times \int d^3k \sum_{l>v} f_{ld^\mu} h_{ld^-}(\omega_0), \quad (17)$$

$$\epsilon_{0,\text{eff}} = \epsilon_{0,v} + (\pi m)^{-1} \left(\frac{e}{\pi}\right)^2 \times \int d^3k \sum_{l>v} f_{ld^\mu} (\omega_{ld}^2 + \tau_{ld}^{-2})^{-1} h_{ld^+}(\omega_0). \quad (18)$$

The first term of Eq. (17) is seen to depend on the same Ω_{Pv}' as that defined by Eq. (7). The last term is

zero until real excitations from the d band are allowed. Thus, n_{eff} differs from the number of valence electrons per atom in this case because of (1) the oscillator strength coupling of the v and d bands, and (2) real transitions taking place between the d and conduction bands. The dielectric constant due to the valence band $\epsilon_{0,v}$ is similarly modified by a term which vanishes until frequencies ω_0 are obtained at which real d -band excitations are possible. It is seen that the last term of Eq. (18), for sufficiently large ω_0 , just corresponds to the quantity involving g_{ld}^R in Eq. (5) with $\omega=0$. This has been written as $\delta\epsilon_0$ in Eq. (6) and assumed to depart little from its value for $\omega=0$. As $\omega_0 \rightarrow \infty$, Eq. (18), therefore, becomes $\epsilon_0 = \epsilon_{0,v} + \delta\epsilon_0$. In this form it is clear that $\delta\epsilon_0$ just represents the contribution of the d electrons to the low-frequency dielectric constant.

When the oscillator strength coupling between the v and d bands vanishes, and the f -sum rule for the valence band is exhausted at an energy lower than $\hbar\omega_{vd}$, then it is possible to identify unambiguously the onset of d -band excitations from a plot of n_{eff} vs $\hbar\omega_0$. Indeed, it is seen from Eq. (17) that such a plot would first saturate at a value of n_{eff} equal to the number of valence electrons per atom and then increase beyond that value when electrons could be excited out of the d band. The term f_{vd} in Ω_{pv} , however, can cause n_{eff} to increase beyond that first saturation value when there is oscillator strength coupling between the v and d bands. These matters were discussed rather inaccurately in reference 7, and will be treated again in the following section in connection with the experimental data.¹⁸

Finally, it should be noted that the same qualitative results are obtained even if the valence band f -sum rule with respect to conduction band states is not quite exhausted. In this case, the correction terms in Eqs. (17) and (18) would involve transitions to highly excited states in the conduction bands as well.

4. DISCUSSION

Region 1

The interpretation of the structure in region 1 has been previously described.⁵ Since this publication, there have been several contributions that provide further information. The work of Brust, Phillips, and Bassani¹⁹ reiterates the importance of critical points in the joint density of states in the interpretation of observed structure,²⁰ and provides the first calculations for such points based on detailed band structure considerations for germanium. This work indicates that structure previously attributed to a single small region of the Brillouin zone, such as the point L , actually

¹⁸ We are indebted to F. Stern for some critical remarks concerning our original discussion.

¹⁹ D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

²⁰ D. T. F. Marple and H. Ehrenreich, Phys. Rev. Letters **8**, 87 (1962).

may be contributed to by an additional critical point elsewhere in the Brillouin zone which, however, is energetically very close. The qualitative aspects of the interpretation given in reference 5, thus, remain the same. In this connection, the importance of considering the dielectric constants themselves, rather than just the reflectance should be emphasized in cases where really accurate analyses are warranted.

The low-temperature reflectance data of Greenaway²¹ for several 3-5 compounds exhibit some additional structure which was not resolvable at room temperature. The structure identified in reference 5 with the $\Gamma_{25'} \rightarrow \Gamma_{15}$ transition in InAs is reassigned by Greenaway to $X_5 \rightarrow X_3$. The former transition is identified with additional structure at 4.63 eV.

Region 2

A. Single Group of Valence Bands

Silicon presents an ideal vehicle for the study of region 2 since d bands are absent in this material and

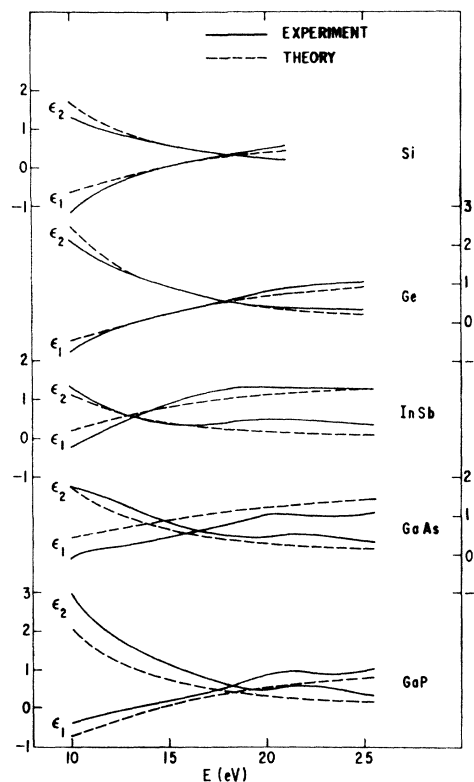


FIG. 4. Experimental and theoretical curves of ϵ_1 and ϵ_2 for Si, Ge, InSb, GaAs, and GaP. The theoretically determined parameters Ω_{pv} and $\delta\epsilon_0$ which are needed for all materials except Si, are given in Table I and Fig. 6, respectively. The adjustable parameter τ_v was taken to be 1.6, 1.4, and 1.8×10^{-16} sec, respectively, for Si, Ge, and InSb. For GaAs and GaP, τ_v was assumed to have the Ge and Si values, respectively. The curve for InAs is similar to that for InSb and has been omitted from this and the following two figures for the sake of brevity.

²¹ D. L. Greenaway, Phys. Rev. Letters **9**, 97 (1962).

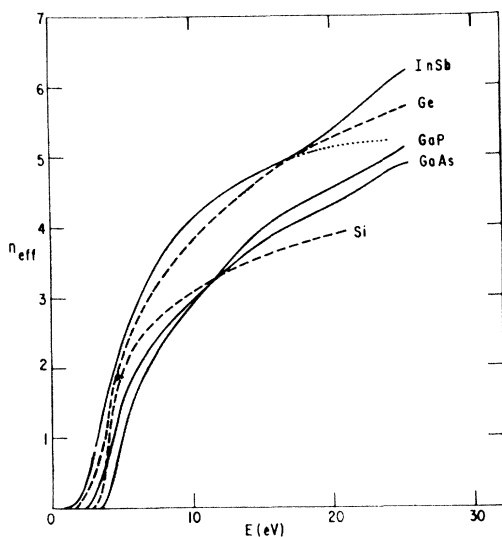


FIG. 5. n_{eff} vs E for group 4 and 3-5 semiconductors. The dotted line represents the extrapolation discussed in the text.

the next filled band lies about 80 eV below the valence bands.¹⁷ Furthermore, the density of states of the valence band as obtained by Hagstrum²² appears to be such that most of the electrons lie within 5 eV of the top of the band, although there is a sparsely populated tail extending to about 16 eV. All of these electrons cannot contribute to the optical properties below photon energies of 16 eV; however, the contribution of the remaining electrons to the dielectric constant is small. Because of the absence of structure related to interband transitions in region 2, Eq. (4) should represent a reasonable description of the dielectric constants in this range. Figure 4 compares experimental and theoretical results for this material. The latter were obtained by taking the plasma frequency ω_{p_v} to correspond to that for four free electrons per atom as prescribed by Eq. (4). The relaxation time τ_v which is assumed constant was determined by matching the experimental and theoretical values of ϵ_2 at the plasma frequency. The magnitude will be discussed subsequently. This Drude-like theory is seen to fit quite well showing that silicon in this range, indeed, behaves essentially like a free electron metal.

B. Semiconductors Containing d Bands

In order to apply the theory outlined in the preceding section, it is necessary to obtain values for the effective plasma frequency Ω_{p_v} and the contribution $\delta\epsilon_0$ of the d bands to the dielectric constant from the experimental data. This is achieved with the help of the modified sum rules given by Eqs. (12) and (13). The prescription for using these relations consists of performing the indicated integrations numerically using the experimental data.

²² H. D. Hagstrum, Phys. Rev. 122, 83 (1961).

The results for the integral given in Eq. (12) are plotted as a function of $E = \hbar\omega_0$ in Fig. 5. It should be noted first that the curve for silicon appears to saturate very nearly at a value of four electrons per atom as expected. The slight overshoot above four is probably due to a small negative contribution to the f sum arising from the core states. By contrast, the curves for germanium and the 3-5 compounds extend appreciably above four. In the case of germanium, n_{eff} increases smoothly with increasing E . For the 3-5 compounds, on the other hand, there is a break in the curve which may be associated with the onset of d -band excitations. The increase above four at lower energies is then evidently associated with the oscillator strength coupling between the valence and d bands. In germanium, the previously mentioned break in the curve is absent because the d band lies considerably deeper.²³ From an extrapolation of the smooth part of the curve, such as that indicated by the dotted curve in the InSb graph, it is possible to estimate the first term, depending on Ω_{p_v}' on the right-hand side of Eq. (17). This procedure is admittedly somewhat crude, but will nevertheless be shown to lead to reasonable results.

A plot of the effective dielectric constant $\epsilon_{0, \text{eff}}$ as a function of $E = \hbar\omega_0$ is shown for several materials in Fig. 6. In addition to providing a good estimate of $\delta\epsilon_0$, a graph of this type is also interesting in that it permits the identification of interband transitions that contribute most importantly to the low-frequency dielectric constant. From the tendency toward saturation at photon energies below 5 eV, it is clear that strong interband transitions at critical points below this energy are mainly responsible for the value of the low-frequency dielectric constant. Transitions near the band gap do not contribute appreciably. The curve for silicon is seen to saturate at a value corresponding to the independently measured low-frequency dielectric

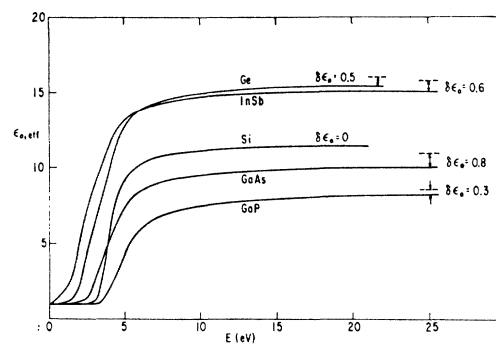


FIG. 6. $\epsilon_{0, \text{eff}}$ vs E for group 4 and 3-5 semiconductors. The low-frequency dielectric constants obtained from reference 13 are indicated by dashed-line segments.

²³ F. Herman and S. Skillman, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Science Publishing House, Prague, 1961), p. 20.

TABLE I. Comparison of plasma frequencies (in eV) as given by free valence electrons (four per atom), the calculations of the present paper, the standard plasma dispersion relation ($\epsilon_1=0$), and the maximum of the energy loss function obtained from optical and electron energy loss experiments.

	ω_{Pv} free electron	Ω_{Pv} eff. freq.	$\epsilon_1(\omega)=0$	$-\max \text{Im}\epsilon^{-1}$ optical	$-\max \text{Im}\epsilon^{-1}$ energy loss
Si	16.6	16.6	15.0	16.4	16.9 ^a
Ge	15.5	16.2	13.8	16.0	16.4 ^b
GaP	16.6	16.3	13.3	16.9	
GaAs	15.5	12.3	9.7	14.7	
InSb	12.7	11.5	10.9	12.0	13.0 ^c

^a See reference 26.

^b See reference 25.

^c B. Gauthé, Phys. Rev. **114**, 1265 (1959).

constant. As expected, there is no contribution from deeper lying bands. By contrast, curves for the remaining materials, which all have d bands, appear to saturate at a value below the independently measured low-frequency dielectric constants¹³ shown here by dashed-line segments. As indicated by the theory of the preceding section, this difference is due just to the contribution of the d bands. The onset of real d -band excitation does not produce a break in the curves for the 3-5 compounds as in the case of the n_{eff} plots since the small increase to the final values is very slow, as indicated by Eq. (18), and extends over many volts. This supports our assumption concerning the frequency independence of $\delta\epsilon_0$.

These results, together with those obtained from Fig. 5, permit the determination of the effective plasma frequency Ω_{Pv} and the contribution of the d bands to the low-frequency dielectric constant. It should be remembered at this point, that this type of analysis depends very sensitively on the absolute values of ϵ_2 and, hence, of the reflectance. Errors in the absolute magnitude of the measured reflectance will produce corresponding errors in the quantities just determined. The preceding cautionary remark may be particularly appropriate for the GaAs results shown in Fig. 5. The difference between these and the Ge results is surprising.²⁴ If indeed real, this difference would indicate a much weaker oscillator strength coupling between the valence and d bands in GaAs.

The effective plasma frequency is compared with the free electron value in Table I. The close correspondence between the two sets of values results from the fact that the quantity $(\frac{1}{4}n_{\text{eff}}/(1+\delta\epsilon_0))$ is close to unity for all these materials with the possible exception of GaAs, whose anomalous character was just described. The remaining columns of the table will be discussed subsequently.

With the values of Ω_{Pv} and $\delta\epsilon_0$ at hand it is now possible to compare the theoretical expression for the

dielectric constant given by Eq. (6) with the experimental values. The only unknown parameter, as before, is the relaxation time. This was assumed constant and determined in the case of Ge and InSb by matching experimental and theoretical values of ϵ_2 somewhere in the range. The results for silicon have already been discussed. A comparison of the theoretical and experimental results is shown in Fig. 4. Good agreement is obtained for Si, Ge, and InSb. The structure in region 3 arising from the d -band excitation, of course, is not included in the present theory and is, therefore, missing from the theoretical curves. In the case of GaP and GaAs, the relaxation times obtained for Si and Ge, respectively, were used. The GaAs results again are somewhat anomalous, but those for GaP are quite reasonable.

It is remarkable that the relaxation times all appear to lie between 1.4×10^{-16} and 1.8×10^{-16} sec. Since the magnitude of the relaxation time is much less than that ordinarily associated with either lattice or impurity scattering, it seems reasonable to suppose that τ is determined by electron-electron scattering. The similarity of the actual values of τ may result from the fact that the band structure on a gross scale for all these materials is rather similar.

C. Plasma Effects

As already pointed out, collective oscillations are described in terms of the longitudinal dielectric constant. In fact, the condition for the existence of plasma oscillations at frequency ω is just $\epsilon(\omega)=0$.¹⁴ This equation, in general, is solved by a complex frequency whose real part corresponds to the plasma frequency and whose imaginary part corresponds to the damping of the plasma resonance. For example, the resonance condition resulting from Eq. (6) is $\omega = \Omega_{Pv} - i/\tau_v$. The relaxation time, thus, describes the damping of the plasma wave.

Much of the experimental information concerning plasma oscillations has come from characteristic energy loss experiments from which one determines the function $-\text{Im}\epsilon^{-1}$.⁹ This function has a maximum at a plasma resonance. Because the longitudinal and transverse dielectric constants should be equal at long wavelengths and the energy loss function $-\text{Im}\epsilon^{-1}$ can be directly calculated from the optical data, it is of interest to compare directly the results of optical and characteristic energy loss experiments. An example of such a comparison for germanium and silicon is shown in Figs. 7(a) and (b), respectively. For Ge, the dashed line represents the characteristic energy loss data of Powell²⁵ for 1.5-keV electrons, and for Si that of Dimigen²⁶ for 47-keV electrons. The energy loss data were normalized so that the peak value of the curve was equal to the maximum of $-\text{Im}\epsilon^{-1}$. The agreement

²⁴ A partial check on the data was made by measuring another sample of GaAs over the range 4-7 eV where the most important contributions to the integrals in question occur. The results for the two samples were found to be in substantial agreement.

²⁵ C. J. Powell, Proc. Phys. Soc. (London) **76**, 593 (1960).

²⁶ H. Dimigen, Z. Physik **165**, 53 (1961).

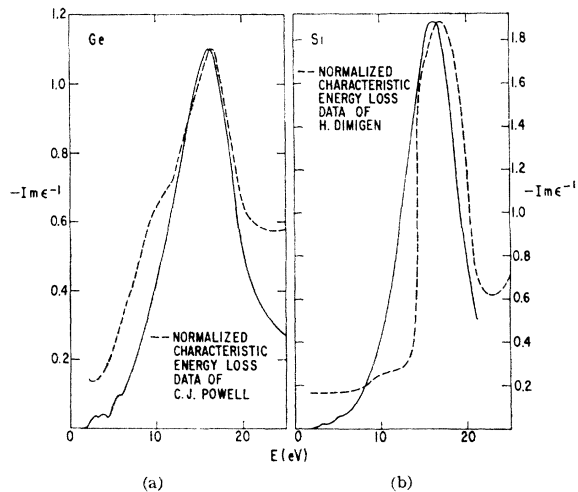


FIG. 7. A comparison of the energy loss function $-\text{Im}\epsilon^{-1}$ obtained from the results of optical and characteristic energy loss experiments for (a) Ge and (b) Si.

in both position and width of the plasma peak in the two cases is very satisfactory. The electron scattering experiments show, in addition, a low-lying loss which is absent in the optical data. This loss is presumably associated with the specimen boundary²⁷ and is without analog in optical data. It is also seen that the Ge data exhibit a further rise at higher energies which is absent in Si. This rise is probably associated with the presence of the d band in Ge.

The energy loss and optical data agree very well in the region where the former is large. It is seen, however, that the energy loss function is rather insensitive to structure in the dielectric constants at low energy. By contrast, the optical constants show only small variations at higher energies.²⁸

The functional form of the dielectric constants in region 2 as given either by Eqs. (4) or (6), is such that the real part ω_{P_r} or Ω_{P_r} of the plasma frequency

²⁷ R. H. Ritchie, *Phys. Rev.* **106**, 874 (1957).

²⁸ Since the function ϵ^{-1} also satisfies the Kramers-Kronig relations, (reference 8) it is possible to analyze characteristic energy loss data in a manner similar to that used here and deduce the dielectric constants. This fact has been previously pointed out by R. LaVilla and H. Mendlowitz [*Phys. Rev. Letters* **9**, 149 (1962)]. Particularly interesting in connection with the present discussion is the fact that the same machine program can be used to perform the Kramers-Kronig analysis for both types of data. The relation between the real and imaginary parts of ϵ^{-1} is given by

$$\text{Re}\epsilon^{-1}(\omega_0) = 1 + (\pi\omega_0)^{-1} \int_0^\infty \left(\frac{d}{d\omega}\right) (\omega \text{Im}\epsilon^{-1}) \ln \left| \frac{\omega + \omega_0}{\omega - \omega_0} \right| d\omega,$$

whereas that between the phase angle θ and the reflectance is as given in the first of references 2. The functional forms of both integrals are the same except that $\ln R$ is replaced by $\omega \text{Im}\epsilon^{-1}$. The principal advantage of an analysis of characteristic energy loss data arises from the fact that such data are much more easily obtainable at higher energies and also that they are more sensitive in this range. On the other hand, it is necessary to subtract out multiple plasma losses and surface effects which may be difficult. For materials like diamond having sufficiently large plasma energies these problems are less acute.

obtained from the relationship $\epsilon(\omega)=0$ agrees with the frequency corresponding to the maximum of the energy loss function to order $1/\omega p^2 \tau^2$. By contrast, the frequency corresponding to $\epsilon_1=0$ agrees with the plasma frequency only to lower order. These facts are substantiated by the entries in Table I, from which it is seen that Ω_{P_v} is in good agreement with the results of the maximum of the energy loss function as obtained from optical and characteristic energy loss experiments. On the other hand, the frequency corresponding to $\epsilon_1=0$ is somewhat displaced. This fact is worth noting since the plasma dispersion relationship applying to a free electron gas is generally stated as $\epsilon_1=0$, ϵ_2 being rigorously 0 at 0°K below the plasma cutoff.²⁹ In an actual solid this idealized situation does not prevail and it is necessary to use the complete equation describing the existence of a plasma oscillation.

Clearly peaks in the energy loss function can be associated either with a plasma oscillation or with interband transitions. As pointed out in a previous paper,⁴ these two physical phenomena can be distinguished rather unambiguously if the dielectric constants in the vicinity of such a peak are known.

The relaxation time τ appearing in Eqs. (4) and (6), which also describes the lifetime of the plasma oscillations, can be estimated from the total width of the peak of the characteristic energy loss function at half maximum. Indeed, one finds that $\Delta\omega/\omega = 2/\omega_{P_v}\tau$. The experimentally observed widths are in good agreement with the values of τ obtained from Fig. 4.

Region 3

It may be useful to recapitulate briefly the reasons for assigning the structure in region 3 to d -band excitations. We observe first that the structure in region 3 present in the 3-5 compounds is absent in Si which does not have a d band and also over the same energy range for Ge, where the d band lies about 30 eV below the top of the valence band.²³ As pointed out previously,⁷ it is the Ga d band which is assigned to the structure observed in GaAs and GaP, and the In d band to the structure in InAs and InSb. In GaP, indeed, the Ga d band is the only one present. In the other 3-5 compounds considered here the cation d bands are more tightly bound. A comparison of the reflectance and dielectric constants appearing in Figs. 1 and 3 shows that the structures in region 3 of the two Ga compounds resemble each other rather closely as do those for the In compounds. This similarity also extends to the absorption coefficients which were discussed in connection with Fig. 2 of reference 7.³⁰

²⁹ See, for example, R. A. Ferrell, *Phys. Rev.* **107**, 450 (1957).

³⁰ The interpretation of the broadening of the d -band absorption edge given in reference 7 must now be questioned in view of the experimental results of R. Deslattes who deduced the lifetime of holes in the In d shell from x-ray emission data on In and InSb and found it much longer than the lifetime previously quoted. The lifetime of a valence band hole-conduction band electron

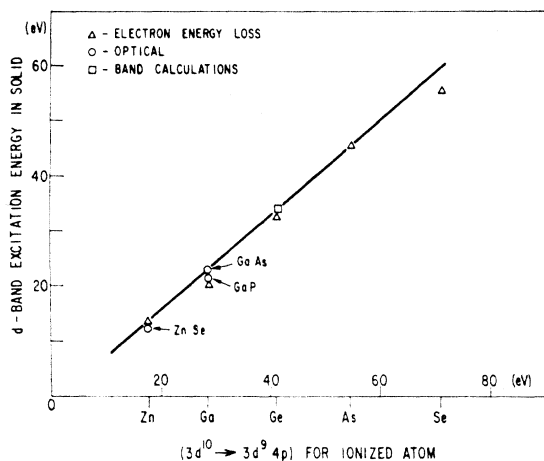


FIG. 8. Energies in various materials attributed to d -band excitations in optical and characteristic energy loss experiments and band calculations vs atomic $3d^{10} \rightarrow 3d^9 4p$ excitation for atoms ionized to the d shell. Unless otherwise indicated, the points refer to the monatomic metals and semiconductors.

Energetically the position of the additional optical structure appears to agree very well with the atomic excitations between the d and lowest unfilled p shells, with energy losses assigned to such excitations, and

pair would be expected to differ from that of a d band hole-conduction band electron pair having the same energy. In particular for an energy close to the onset of region 3 the lifetime in the first case would be determined by the excited electron, and in the latter case by the excited hole. It may be that the observed structure in the dielectric constants is actually a convolution of transitions at different points of the Brillouin zone rather than a single dominating interband transition to which this structure was tacitly attributed in reference 7. We wish to thank Dr. Deslattes for communicating his results prior to publication.

with band calculations where available. Figure 8 summarizes the available information concerning such excitations for a horizontal sequence in the periodic table which also includes Ge. This figure shows a plot of the energy that has been either experimentally or theoretically attributed to d -band excitation in solids containing the atoms listed on the abscissa as a function of the d -band excitation energy of the ionized atom stripped to the d shell. This means that we consider the $3d^{10} \rightarrow 3d^9 4p$ transitions in ZnIII, GaIV, GeV, etc.³¹ The figure considers characteristic energy loss data for the monatomic metals,³² optical data for the indicated compounds, and the results of Herman's calculations for Ge.²³ The energy for this transition should not be affected seriously on the above energy scale, when the ion is embedded in different solids. Thus one would anticipate a reasonable correlation between the two quantities plotted here if the identification of the d -band excitations is correct. Figure 8 indeed exhibits this correlation. Similar arguments can be made for the indium compounds.

ACKNOWLEDGMENTS

During the course of this work, we have profited from discussions with a number of colleagues. Among these we thank, in particular, L. Apker, W. C. Dash, P. Martin, J. C. Phillips, F. Stern, and E. A. Taft. We are also grateful to Doris J. Olechna for her capable help with the numerical calculations.

³¹ C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, 1949).

³² J. L. Robins, *Proc. Phys. Soc. (London)* **79**, 119 (1962).