

the $\text{Li}_{31}\text{Mg}_{19}$ specimen the surface probably bulges and may touch the zone boundary. If the nearly free-electron theory (two plane waves) is applicable, the bulge would result in an appreciable tail above k_{ZB} and some diminution below k_{ZB} but still above k_f , the free-electron radius. Thus the cutoff should be sharper on the lower side and more gradual on the higher momentum side. The opposite is observed. In the $\text{Li}_{42}\text{Mg}_{58}$ specimen the smear caused by the zone boundary should be approximately symmetric about k_f . The data show a strong asymmetry which is thus still unexplained.

One effect of alloying the two metals could be to smear the Fermi surface in the manner described by Edwards⁹ for spatial disorder in liquids. Such smearing should also be symmetrical, however, and thus cannot account in full for these data.

We are finally led to speculate that the shape of the cutoff is influenced by the alloy nature of the metal but in another way. We suggest that the pile up of electric

charge around the magnesium ions must be described by electron wave functions which have Fourier components widely dispersed through k space. These higher momentum components are not easily "seen" in this experiment. The resultant diminution in occupation of k space within the Fermi surface seems to occur preferentially for $k \gtrsim \frac{2}{3}k_{\text{ZB}}$, this being the maximum value of k for which the linear relation is observed in the figure. It is not unreasonable to suppose that those electrons with a half-wavelength approximately equal to an atomic spacing are the ones required to heap up charge around the Mg^{++} ions. We hope that this speculation can be checked by a calculation of electron wave functions in such a metal alloy.

ACKNOWLEDGMENTS

We have profited by helpful discussions with colleagues at Chapel Hill and with Dr. Oliver LeBlanc and Dr. Philip Taylor, and are indebted to J. H. Kusmiss, J. J. Donaghy, and J. B. Shand for technical assistance.

⁹ S. F. Edwards, Proc. Roy Soc. (London) **A267**, 518 (1962).

Dispersion of the Index of Refraction Near the Absorption Edge of Semiconductors*

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A simple method is used to calculate the contribution of the rapid rise in optical absorption near the absorption edge of semiconductors to the index of refraction near the edge. Other contributions to the index are also estimated. The results give qualitative agreement with the results obtained for PbS by Riedl and Schoolar, and very good agreement with Marple's prism measurements of the index for GaAs. Some applications to injection lasers are discussed. The temperature and pressure dependence of the index of refraction near the absorption edge is estimated, and agrees well with experimental results for GaAs.

I. INTRODUCTION

THE absorption edge of a semiconductor is usually a region of very rapidly rising absorption. It is a direct consequence of the dispersion relation¹ between the real and imaginary parts of the complex index of refraction that this rapid rise in absorption will lead to structure in the index of refraction near the photon energy of the absorption edge. We shall examine this structure using both numerical absorption data and a number of simple models for the absorption near the edge. We find that there is rapid dispersion of the index of refraction near the edge, and in some cases a peak in the index. However, the total variation of the index near the absorption edge is small in the semiconductors

which we consider. For that reason the effect has only occasionally² been considered in detail heretofore.

The development of injection lasers, which have narrow emission lines near the absorption edge, has provided a sensitive tool for studying the dispersion of the index of refraction near the edge, and has motivated this work. The application to lasers is discussed specifically in Sec. V. In Sec. II we give the relevant dispersion relations, and show how they can most conveniently be used to treat the variation of the index near the absorption edge. In Sec. III we present a number of simple models, and in Sec. IV we apply these methods to obtain results for GaAs and PbS which are in fair to excellent agreement with experiment. In the last section, we show how the same methods used to describe the dispersion of the index also give a good description of the effect of temperature or pressure

* A brief account of this work was presented at the St. Louis meeting of the American Physical Society, in March 1963 [Bull. Am. Phys. Soc. **8**, 201 (1963)].

¹ See, for example, F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 327.

² T. S. Moss, S. D. Smith, and T. D. F. Hawkins, Proc. Phys. Soc. (London) **B70**, 776 (1957).

changes on the index near the edge, and compare some approximate predictions of our model with experimental results.

We shall describe the optical properties of semiconductors either in terms of the index of refraction n and the extinction coefficient k , or in terms of the complex dielectric constant

$$\kappa_1 + i\kappa_2 = (n + ik)^2, \quad (1)$$

where we assume throughout that the medium is non-magnetic. The reflectivity is given in terms of n and k by

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2], \quad (2)$$

and the extinction coefficient is related to the absorption coefficient α by

$$k = \alpha\lambda/4\pi = c\alpha/2\omega = \hbar c\alpha/2E \\ = 0.980 \times 10^{-5} \alpha [\text{cm}^{-1}] / E [\text{eV}], \quad (3)$$

where λ , ω , and E are the vacuum wavelength, the angular frequency, and the photon energy, respectively, of the radiation. In most cases the extinction coefficient will be small or negligible in Eq. (2), and we find, to lowest order in k^2 , that

$$n \approx \frac{1 + R^{1/2}}{1 - R^{1/2}} \left[1 - \frac{k^2(1 - R^{1/2})^2}{4R^{1/2}} \right]. \quad (4)$$

II. APPLICATION OF DISPERSION RELATIONS

The behavior of the index of refraction can be deduced, if the extinction coefficient is known for all values of photon energy, from the dispersion relation¹

$$n(E) - 1 = (2/\pi) \int_0^\infty E' k(E') [E'^2 - E^2]^{-1} dE', \quad (5a)$$

which can be cast in the equivalent forms

$$n(E) - 1 = (\hbar c/\pi) \int_0^\infty \alpha(E') [E'^2 - E^2]^{-1} dE', \quad (5b)$$

$$n(E) - 1 = (\hbar c/2\pi E) \int_0^\infty [d\alpha(E')/dE'] \\ \times \ln[(E' + E)/(E' - E)] dE'. \quad (5c)$$

Equation (5c) can be derived from (5b) by integration by parts if $E\alpha(E) \rightarrow 0$ as $E \rightarrow 0$ and $\alpha(E)/E \rightarrow 0$ as $E \rightarrow \infty$. These conditions are required for convergence of the integrals in (5), and will hold for all cases we consider. The coefficient of the integral in (5b) equals 6.28×10^{-6} if α is given in units of cm^{-1} and E is expressed in eV. The coefficient of the integral in (5c) equals $\lambda/4\pi^2$.

Dispersion relations allow us to transform the problem of determining the behavior of the index of refraction to the problem of finding the behavior of the

absorption coefficient. Fortunately, we have experimental data for the absorption coefficient near the absorption edge of most semiconductors, and we can in many cases determine its behavior at higher energy from analysis of reflectivity measurements.³

Equation (5c) shows that the largest contributions to the index of refraction come from energy regions in which the absorption is varying rapidly. Such regions are associated with peaks and other structure in the reflectivity, such as is found in GaAs at about 3 and 5 eV.³⁻⁵ It would be simplest if the absorption coefficient could be represented as the sum of a number of sharp peaks, since these would give a very simple contribution to the index of refraction via Eq. (5b). Unfortunately the experimental results cannot be characterized very well by sharp peaks in $\alpha(E)$. We can, however, characterize the absorption of many semiconductors at energies above the energy gap by one or more sharp peaks in κ_2 , the imaginary part of the dielectric constant.

We are therefore forced to combine information about the absorption coefficient near the absorption edge with information about the imaginary part of the dielectric constant at higher photon energies to get a simple model of the dispersion of the index of refraction near the absorption edge. This is most easily done if we use the dispersion relation for the dielectric constant¹:

$$\kappa_1(E) - 1 = (2/\pi) \int_0^\infty E' \kappa_2(E') [E'^2 - E^2]^{-1} dE'. \quad (6)$$

If we represent the high-energy peaks in κ_2 by delta functions:

$$\kappa_2(E) = \sum_j (\pi G_j/2E_j) \delta(E - E_j), \quad E > E_s, \quad (7)$$

and assume that we know the absorption coefficient for energies less than the arbitrarily chosen energy E_s , which separates the "high"-energy region from the "low"-energy region, we can write the dispersion relation for the dielectric constant in the form

$$n^2 - k^2 - 1 = (4/\pi) \int_0^{E_s} n(E') k(E') [E'^2 - E^2]^{-1} dE' \\ + \sum_j G_j [E_j^2 - E^2]^{-1}. \quad (8)$$

Equation (8) is an integral equation which implicitly determines the index of refraction if we know the constants E_j and G_j and the extinction coefficient $k(E')$, which is related to the absorption coefficient by Eq. (3). The

³ H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963). I am indebted to Dr. Philipp and Dr. Ehrenreich for a preprint of this paper.

⁴ J. Tauc and A. Abrahám, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 375.

⁵ R. E. Morrison, Phys. Rev. **124**, 1314 (1961).

approximations we use are valid only for photon energies $E < E_s$, and we apply Eq. (8) only in this energy range.

Equation (8) is easily solved numerically by successive approximations. As a first approximation we can neglect the integral in (8), and find

$$n_0(E) = [1 + k^2(E) + \sum G_j(E_j^2 - E^2)^{-1}]^{1/2}. \quad (9)$$

This approximate result can then be substituted in the integral in (8) to obtain a second approximation. The procedure converges quite rapidly. For example, in the numerical calculations for GaAs to be described in Sec. IV, the maximum index difference between the second and third iterations of Eq. (8) was less than 0.0001 for any value of E . Some details of the numerical integration are described in the Appendix.

An estimate of the contribution of the absorption edge region to the dispersion of the index can be obtained from Eq. (5b) if we integrate only over the absorption edge itself. We find

$$\Delta n(E) \approx (\hbar c / \pi) \int_0^{E_s} \alpha(E') [E'^2 - E^2]^{-1} dE', \quad (10)$$

where E_s is, as in (8), an arbitrary energy separating the region near the edge from the high-energy region. We have simplified the procedure by requiring that $\alpha(E)$ go to zero at $E = E_s$. Fortunately, in GaAs and the other semiconductors to which we apply our method, it is possible to choose a value of E_s which is well above the absorption edge, and also lies below the energies E_j of the peaks in the imaginary dielectric constant. Thus, our approximations should be adequate to give a good description of the index of refraction near the absorption edge. The coefficient of the integral in (10), as in (5b), equals 6.28×10^{-6} cm-eV if α and E are expressed in cm^{-1} and eV, respectively.

We have found in the case of GaAs that the approximate expression (10) somewhat underestimates the difference between the index of refraction as found from repeated application of Eq. (8) and the first approximation given by (9). In a material in which the contribution of the absorption edge is relatively more important than in GaAs, it might be desirable to use the sum of (9) and (10) as the first approximation in the iterative solution of (8), to speed the convergence.

III. CONSIDERATION OF SPECIFIC MODELS

Equation (8) allows us to combine accurate information for the absorption edge with approximate expressions for the losses at higher photon energy to find the index of refraction near the absorption edge. Where experimental data for the absorption edge are available, we need only substitute these in Eq. (8), and choose appropriate values of the parameters E_j and G_j . It often happens that complete absorption data are not available, because of the difficulty of preparing the very thin specimens needed to measure high-absorption

constants and of protecting them against strains and breakage, particularly for measurements far from room temperature. We shall therefore consider some simple models for the shape of the edge and discuss their contribution to the index of refraction. Some smaller contributions to the index are also discussed.

Parabolic Bands

The simplest case to describe is the conventional absorption edge arising from allowed direct transitions between conduction and valence bands, for which we write the absorption coefficient in the form

$$\alpha(E) = 0, \quad E < E_g, \quad (11a)$$

$$\alpha(E) = B(E - E_g)^{1/2} [1 - (E - E_g)(E_s - E_g)^{-1}], \quad E_g < E < E_s. \quad (11b)$$

The bracketed factor in (11b) is an artificial damping factor used to assure that $\alpha(E)$ goes to zero at $E = E_s$, since this is required to simplify the separation of the high-energy and low-energy regions in Eq. (8). As long as E_s is not too close to E_g , the final results will not be sensitive to the value of E_s .

If we let $E_s \rightarrow \infty$, we find from Eq. (10) that⁶

$$\Delta n(E) = (\hbar c B / 2E) [(E_g + E)^{1/2} - (E_g - E)^{1/2}], \quad E < E_g, \quad (12a)$$

$$= (\hbar c B / 2E) (E_g + E)^{1/2}, \quad E > E_g. \quad (12b)$$

We see that there is a peak in the index of refraction at the absorption edge and that dn/dE has an inverse square-root singularity at the edge. In a more realistic model in which the abrupt rise in $\alpha(E)$ near $E = E_g$ is softened by the absorption tails which are always present,⁷ and in which the deviation from the square-root behavior at higher energies is taken into account, we find that the index peak will be slightly shifted in energy, and that the singularity in dn/dE will be removed. The gross behavior of the index of refraction near the absorption edge will still be given by Eq. (12).

Exponential Band Edge

If the Coulomb interaction between the electron and the hole produced by absorption of a photon is taken

⁶ See also L. I. Korovin, *Fiz. Tver. Tela* **1**, 1311 (1959) [English transl.: *Soviet Phys.—Solid State* **1**, 1202 (1960)]. [Note added in proof. Korovin uses the conventional (Ref. 1) expression $\alpha(E) \sim (E - E_g)^{1/2}/E$, which applies to allowed transitions between parabolic bands if the matrix element is constant, and obtains a result somewhat different from Eq. (12). In real crystals, nonparabolicity and matrix element changes become important when $E - E_g$ is no longer small compared to E_g . Optical absorption data for the lead salts (Ref. 33) and for InAs (J. R. Dixon and J. M. Ellis, *Phys. Rev.* **123**, 1560 (1961)) are consistent with Eq. (11b) if $E_s \gg E_g$, but not with the conventional expression. I am indebted to Dr. M. Cardona for a discussion.]

⁷ See, for example, F. Stern, *J. Appl. Phys.* **32**, 2166 (1961).

into account,^{8,9} the absorption near the edge will differ substantially from the square-root behavior given by simpler considerations. Under conditions in which bound exciton states exist, there will be distinct peaks in the absorption at energies below the absorption edge. We will discuss the behavior of the index of refraction associated with such absorption peaks below, and here restrict our attention to the case in which discrete exciton transitions are not observed, either because the thermal energy KT exceeds the exciton binding energy, or because screening effects have pushed the exciton levels into the continuum.¹⁰ In such cases the theory^{8,9} predicts a rapid rise in absorption, followed by a gradual approach to the absorption values that would be obtained without considering Coulomb interaction.

Experimentally it is often found that the absorption constant can be represented over one or more decades by an exponential dependence on the energy.⁷ In the numerical calculations we have assumed that the absorption constant takes the form:

$$\alpha(E) = A \exp[(E - E_c)/E_l], \quad E < E_c, \quad (13a)$$

$$\alpha(E) = A[1 + (E - E_c)/E_r - (E - E_c)^2/E_r E_s], \quad E_c < E < E_s, \quad (13b)$$

in which E_l and E_r describe the behavior of the absorption in the immediate neighborhood of the edge, and $E_s = (E_g - E_c)^2/(E_s + E_r - E_c)$ is chosen to make the absorption vanish at E_s . When the absorption edge is given by (13), we find from Eq. (10) that the leading terms describing the variation of the index of refraction near the edge are

$$\Delta n(E) = \frac{A\lambda_e}{4\pi^2} \left\{ \ln \left(\frac{E_s - E_c}{E_c - E} \right) + \exp \left(\frac{E - E_c}{E_l} \right) \text{Ei} \left(\frac{E_c - E}{E_l} \right) \right\}, \quad (14)$$

where λ_e is the wavelength in vacuum corresponding to energy E_c , and $\text{Ei}(x)$ is the exponential integral.¹¹ The expression in braces in (14) has its peak when $E = E_c - 0.37E_l$; the peak in the index derived from Eq. (8) will usually be shifted slightly in energy.

The parameter E_l which characterizes the steepness of the absorption edge will be strongly influenced by both temperature and composition, and the dispersion of the index near the edge will thus be influenced by these factors. Both increasing temperature and increasing impurity content tend to broaden the ab-

sorption edge, and will therefore tend to reduce the dispersion of the index near the edge.

Absorption Peaks

In some cases the absorption coefficient may show distinct peaks or dips, such as the exciton peaks which are seen in the absorption of many pure semiconductors at low temperatures. We shall discuss this case only approximately, and shall not attempt to give a quantitative account which would be necessary to describe, say, alkali halides, in which the exciton peaks dominate the absorption spectrum.¹²

A simple model of a symmetrical peak is one for which the contribution to the complex index of refraction is given by $C/(E_0 - E - ig)$. The absorption coefficient is

$$\alpha = 4\pi k/\lambda = (4\pi Cg/\lambda)[(E_0 - E)^2 + g^2]^{-1} \quad (15a)$$

and the contribution to the index of refraction is

$$\Delta n = C(E_0 - E)[(E_0 - E)^2 + g^2]^{-1}. \quad (15b)$$

If $g \ll E_0$, the index contribution (15b) will have extrema at $E \pm g$, and the maximum excursion of the index is one-half of the height of the extinction-coefficient peak. When the absorption-coefficient peak is positive, the index has a positive excursion on the low-energy side of the peak, and a negative excursion on the high-energy side. For a negative absorption change, these directions are reversed. If the change in the extinction coefficient is not symmetrical, the excursion of the index on the steeper side will be more pronounced than one would estimate from (15b), and the excursion on the other side will be less pronounced or absent altogether.

Indirect Absorption Edge

When the absorption at the optical energy gap is indirect, requiring a phonon to provide the momentum difference between the bottom of the conduction band and the top of the valence band, or when the transition is not allowed, the rise in absorption will be slower than that given by Eqs. (11) or (13).⁹ In such cases the associated dispersion in the index would be much less pronounced than for the cases we have considered, and a peak in the index of refraction is unlikely to occur near such an edge. In Ge and Si, for example, the transitions at the lowest energy gap are indirect, and we expect the first major structure in the index of refraction to occur near a higher energy gap or other critical point in the energy difference between conduction and valence bands.

Free Carriers

Two other loss mechanisms which affect the index of refraction near the absorption edge are free-carrier

⁸ R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

⁹ T. P. McLean, in *Progress in Semiconductors*, edited by A. F. Gibson (Heywood and Company, Ltd., London, 1960), Vol. 5, p. 53.

¹⁰ R. C. Casella, J. Appl. Phys. **34**, 1703 (1963). I am indebted to Dr. Casella for a preprint of this paper.

¹¹ The product $\exp(-x) \text{Ei}(x)$ has been tabulated by J. Miller and R. P. Hurst, Math. Tables Aids Comput. **12**, 187 (1958).

¹² See, for example, J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

absorption, and interaction with lattice vibrations. In most cases these can also be represented to sufficient accuracy by delta-function peaks in the imaginary part of the dielectric constant, which, in the notation of Eq. (7), leads to

$$\Delta n_j = (G_j/2n)(E_j^2 - E^2)^{-1}. \quad (16)$$

For the intraband transitions of free carriers we find

$$E_{\text{intra}} = 0, \\ G_{\text{intra}}[\text{eV}^2] = 1.38 \times 10^{-21} N[\text{cm}^{-3}](m/m^*), \quad (17)$$

where N is the concentration of free carriers and m^* is their susceptibility mass.¹³ If several groups of carriers of different masses are present, we must add their contributions to find the total G_{intra} .

If interband transitions involving free carriers are present, they will also contribute to the dispersion. The principal contribution in p -type samples will be the transition between the light- and heavy-hole bands, which is prominent in GaAs,¹⁴ InAs,¹⁵ and especially so in InSb.¹⁶ Interband transitions of free carriers have also been observed in n -type GaAs,¹⁷ p -type PbTe,¹⁸ and other semiconductors.⁷

No simple expression can be given to describe the interband effects, and estimates of their magnitude must be based on experimental absorption data in each case. We consider the case of GaAs as an example in Sec. IV.

Lattice Vibrations

The dispersion associated with lattice vibrations can be represented, again in the notation of Eq. (7), in the form:

$$E_{lv} = E_T, \quad G_{lv} = (\kappa_s - \kappa_\infty)E_T^2, \quad (18)$$

where E_T is the energy of the transverse optical lattice vibration modes of long wavelength, and κ_s and κ_∞ are the limiting values which the dielectric constant approaches well below and well above E_T when the free-carrier contribution is ignored. This loss term leads, via Eq. (6), to the usual form for the dispersion of the dielectric constant of an ionic crystal.¹⁹ In discussing the dispersion of the optical constants near the absorption edge of semiconductors we can usually let $E_{lv} = 0$. The lattice vibration contribution to the index of refraction at the absorption edge is negligible in materials with a large energy gap, as can be seen in the estimate to be made below for GaAs in Table II, but may need to be considered in small-gap semiconductors.

Of the contributions to the dispersion of the index of

refraction near the absorption edge which have been mentioned in this section, only the first three will give a rapid variation of the index near the edge. The variation is confined to a relatively narrow range of energies, and thus the total variation of the index may be small. Indeed, reflectivity measurements generally do not have a noticeable peak near the first absorption edge, but instead show reflection peaks at higher energies³ which are connected with transitions for which the absorption changes are larger, and for which the corresponding index and reflectivity changes are therefore more pronounced.

Experimental observations of the rapid dispersion of the index of refraction near the optical absorption edge have been made by a prism method for GaAs,²⁰ by multiple interference methods for GaAs,²¹ InSb,² and PbS,²² by ellipsometry for GaAs,²³ and by reflection for InSb,⁵ PbS,²² and ZnSe.²⁴ The list could certainly be extended. The prism method, which gives very precise values of the index, cannot detect a peak near the absorption edge because the material absorbs too strongly there. The multiple interference method will be similarly limited when thick samples are used. All the other measurements we have mentioned have reported the existence of an index peak. We shall compare experimental results for GaAs and PbS with calculated values in the following section.

IV. NUMERICAL RESULTS FOR GaAs AND PbS

Gallium Arsenide

We have applied the methods described in the previous sections to determine the index of refraction near the absorption edge of GaAs. The most direct comparison with experiment is possible for pure²⁵ GaAs, for which absorption data over the required range²⁶ and precise index measurements²⁰ are available at a number of temperatures.

The exponential band edge approximation of Eq. (13) represents Sturge's absorption data²⁶ quite well, and was used to calculate the index of refraction at 103°K and at 298°K. These temperatures represent the extremes of the range covered in Marple's prism measurement.²⁰ The parameters of Eq. (13), as obtained from Sturge's results with some interpolation, are listed in Table I, as are the nominal values used for the energies of the peaks in the imaginary part of the dielectric

²⁰ D. T. F. Marple (to be published).

²¹ M. I. Nathan, A. B. Fowler, and G. Burns, Phys. Rev. Letters **11**, 152 (1963).

²² H. R. Riedl and R. B. Schoolar, Phys. Rev. **131**, 2082 (1963).

²³ R. J. Archer (unpublished). I am indebted to Dr. Archer for informing me that he has observed a peak in the index of refraction of GaAs at the absorption edge.

²⁴ M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. **32**, 2261 (1961).

²⁵ By "pure" we mean that the content of impurities and other imperfections is small enough to have a negligible effect on the optical constants near the absorption edge.

²⁶ M. D. Sturge, Phys. Rev. **127**, 768 (1962).

¹³ W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).
¹⁴ R. Braunstein, Phys. Chem. Solids **8**, 280 (1959).
¹⁵ F. Matossi and F. Stern, Phys. Rev. **111**, 472 (1958).
¹⁶ G. W. Gobeli and H. Y. Fan, Phys. Rev. **119**, 613 (1960).
¹⁷ W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959).
¹⁸ H. R. Riedl, Phys. Rev. **127**, 162 (1962).
¹⁹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1956), p. 83.

TABLE I. Numerical values used for the calculated curves of Figs. 1-4. Column 2 gives the equations in the text in which each quantity is defined or used.

Quantity and units	Equation	Fig. 1		Fig. 2	Fig. 3	Fig. 4
		GaAs 103°K	GaAs 298°K	GaAs 300°K	PbS 300°K	GaAs 2°K
E_1 [eV]	(7,8)	3.1	3.0	3.0	3.7	3.13
G_1 [eV ²]	(7,8)	36.0	34.7	34.7	200.0	36.39
E_2 [eV]	(7,8)	5.1	5.0	5.0	...	5.13
G_2 [eV ²]	(7,8)	145.37	142.43	142.43	...	146.25
A [cm ⁻¹]	(13)	8700	7900	7900 ^a	...	8940
E_c [eV]	(13)	1.500	1.425	1.425 ^a	...	1.52
E_i [eV]	(13)	0.0028	0.0067	...	...	0.010
E_r [eV]	(13)	0.15	0.15	0.15 ^a	...	0.15
E_s [eV]	(11,13)	2.91	2.86	2.86 ^a	3.0	2.925
B [cm ⁻¹ eV ^{-1/2}]	(11)	...	...	...	3.44×10 ⁴	...
E_g [eV]	(11)	...	...	...	0.41	...

^a These values are used only above 1.64 eV.

constant,³ with crude allowance for their temperature dependence.^{27,28}

Our calculated values of the index of refraction, and some of Marple's prism data,²⁰ are shown in Fig. 1. The values of the parameters G_j which are used are listed in Table I. These two constants essentially fix the value of the index at low energies and its rate of change with E^2 , and were determined by fitting Marple's data. In making this fit a small correction ($\Delta n < 0.001$) for the lattice-vibration and free-carrier contributions to the index was made, using the estimated electron concentration, $N \approx 6.5 \times 10^{16}$ cm⁻³, of Marple's prism material. Numerical expressions for these corrections are given later in this section.

The maximum difference between the calculated and observed index values is 0.002 at 103°K and 0.004 at 298°K. This error would have been greater by at least a factor of 10 had we not included the contribution of the absorption edge in the calculation, which shows that the rapid rise in absorption makes an important con-

tribution to the index of refraction near the absorption edge of GaAs.

To see whether the empirical parameters G_j which were used to fit Marple's data are at all reasonable, we have compared the integrated heights of the 3- and 5-eV peaks in the imaginary dielectric constant as determined by Philipp and Ehrenreich³ with the corresponding values that follow from the model of Eq. (7) and the numerical values for 298°K in Table I. The experimental values for $\int \kappa_2 dE$ are about 18 and 25 eV, respectively, for the two peaks, while the values in Table I give 18.2 and 44.7 eV, respectively. Thus, the 3-eV peak is represented very well by our empirical fit. The empirical 5-eV peak is too high because it must include the contributions of κ_2 at all higher energies. About half of the discrepancy is accounted for by the observed peak at 6.3 eV, which is not included in our model. The empirical and the observed values are thus in satisfactory agreement.

From the parameters used to calculate the curves in Fig. 1, we estimate that the extrapolated index of refraction of GaAs at long wavelengths, without the free-carrier or lattice-vibration contributions, is 3.263 at 103°K and 3.297 at 298°K.

Some of the features of the calculated curves in Fig. 1 cannot be compared with Marple's data, since the prism method can only be used in spectral regions in which the prism transmits light. The calculations show that the index will have a peak just below the energy of the corner where the rapid rise in absorption ends, and will then fall to a broader minimum before resuming its rise. The difference between the calculated maximum and minimum values is 0.041 at 103°K and 0.026 at 298°K. The peak is exaggerated somewhat by our absorption model, with its sharp corner at the energy E_c of Eq. (13), but the presence of the peak, and its greater narrowness and height at lower temperature, should be preserved in a more realistic treatment. The

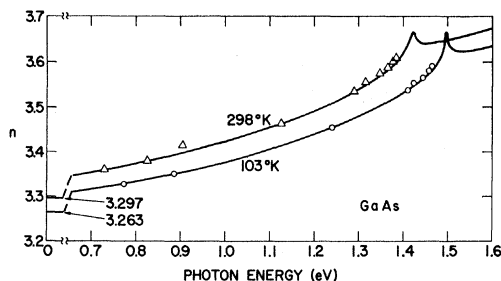


FIG. 1. Index of refraction of relatively pure GaAs. The curves are calculated using Eq. (8) and the parameters listed in Table I. The points are taken from the prism measurements of Marple (Ref. 20). The indicated values at zero photon energy are the long-wavelength limits of the index at 103°K and 298°K in the absence of the lattice-vibration and free-carrier contributions.

²⁷ D. L. Greenaway, Phys. Rev. Letters **9**, 97 (1962).

²⁸ M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963).

existence of a peak in the index of refraction of GaAs at the absorption edge has been confirmed at room temperature by ellipsometric methods,²³ but detailed comparison with the calculated curve is not possible at present. The reflectivity rise observed by Greenaway²⁷ at 80°K is too large, and falls too far below the absorption edge, to correspond to the peak in the calculated index curves.

The exciton peak in the low-temperature absorption data for GaAs²⁶ will lead to some additional dispersion in the index of refraction. We estimate from Sturge's data that at 103°K the peak is 1700 cm⁻¹ high and 0.005 eV wide, and that it is steeper on the low-energy side. According to Eq. (15), this should contribute about 0.006 to the index of refraction 0.0025 eV below the energy of the exciton peak, and a smaller negative amount just above the peak. Thus, the contribution of the exciton peak to the index of refraction is rather small for GaAs, but it would be much more important in materials such as ZnSe²⁴ and the alkali halides,¹² where the exciton absorption is more pronounced.

In impure samples differences in the shape of the absorption edge, and free-carrier effects, will lead to differences in the index from the value found in pure material. To illustrate these effects we have used the data of Kudman and Seidel²⁹ on optical absorption of *p*-type GaAs at 300°K to calculate the dispersion of the index near the edge. Their curves cannot be represented well by an exponential approximation like that of Eq. (13), so the numerical values from the curves of Kudman and Seidel were used, and were freely extrapolated so as to join smoothly onto the absorption constant of Eq. (13b), which was used in the energy range above 1.64 eV. The same values of the constants E_j and G_j were used as for the room-temperature case in Fig. 1, although one can expect these values to change somewhat in very impure samples.³⁰ The values of the parameters are listed in Table I, and the resulting values of the index of refraction for a small energy range near the absorption edge are shown in Fig. 2.

A number of qualitative features of the index curves are apparent. Only the purest of the five samples shows a peak in the index of refraction. The absence of a peak in the other four curves is not surprising in view of the more gradually rising absorption in the impure samples. The index curve for the purest sample in Fig. 2 is in fairly good agreement with the room-temperature curve in Fig. 1. The principal difference between the curves is a somewhat less pronounced index peak in Fig. 2, which is to be expected since the Kudman-Seidel²⁹ absorption data are somewhat more rounded than Sturge's²⁶ data.

The curves of Fig. 2 do not include the contributions of lattice vibrations or of free carriers to the index of refraction. The lattice vibration contribution is given

by Eq. (18), where we take $E_T=0.033$ eV³¹ and $\kappa_s-\kappa_\infty=1.63$,³² from which $G_{lv}=1.8\times 10^{-3}$ eV². Thus, near the absorption edge of GaAs, if E is the photon energy in eV,

$$\Delta n_{lv}(E) \approx -9 \times 10^{-4} / n E^2, \quad (19)$$

since E_T can be neglected in comparison with E in Eq. (16). The coefficient in (19) was obtained from room-temperature data^{31,32} but we use the result at lower temperatures also.

The intraband free-carrier absorption of holes in GaAs leads, via Eqs. (16) and (17), to $G_{intra}=3.7 \times 10^{-21}P$, where P is the number of holes per cm³, and to

$$\Delta n_{intra}(E) \approx -1.8 \times 10^{-21}P / n E^2. \quad (20)$$

To obtain this result we assumed that the light and heavy holes had effective masses 0.12 m and 0.5 m , respectively, and that their concentrations were proportional to the 3/2 power of their masses. Because of the uncertainty in the hole masses, the coefficient in (20) may be in error by as much as 50%.

The interband contribution to the free-carrier absorption of *p*-type GaAs is hard to estimate quantitatively because the major contribution comes from the transitions between light and heavy hole bands at long wavelengths, for which the data¹⁴ are incomplete and for which the contributions of interband and intraband processes cannot be clearly separated. We have nevertheless made a crude estimate, using Braunstein's data at 295°K, that the integrated interband free-carrier absorption is $\int \alpha(E) dE \approx 10^{-16}P$ cm⁻¹ eV. Because of departures from parabolicity for the light hole band, and because of the degeneracy of the holes at high concentrations, we do not expect this estimate to be even approximately valid beyond $P \approx 10^{19}$ cm⁻³ at

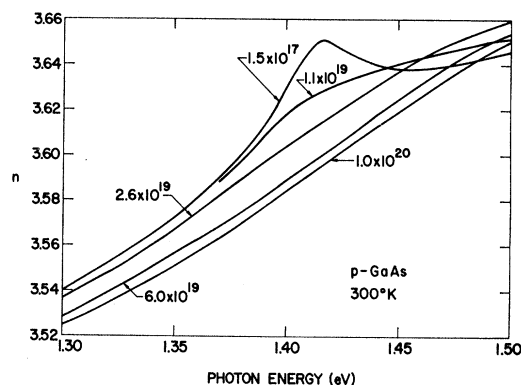


Fig. 2. Index of refraction of *p*-type GaAs at 300°K, calculated from the optical absorption data of Kudman and Seidel (Ref. 29) and the parameters listed in Table I. The lattice-vibration and free-carrier contributions to the index have not been included in the curves (but see Table II).

²⁹ I. Kudman and T. Seidel, J. Appl. Phys. **33**, 771 (1962).

³⁰ M. Cardona and H. S. Sommers, Jr., Phys. Rev. **122**, 1382 (1961).

³¹ G. Picus, E. Burstein, B. W. Hennis, and M. Hass, Phys. Chem. Solids **8**, 282 (1959).

³² K. G. Hambleton, C. Hilsum, and B. R. Holeman, Proc. Phys. Soc. (London) **77**, 1147 (1961).

TABLE II. Calculated index of refraction at 300°K and a photon energy of 1.37 eV for the two purest samples of Fig. 2. The first column gives the hole concentration, and the second column gives the index of refraction as calculated from Eq. (8) using the optical-absorption data of Kudman and Seidel (Ref. 29) and the parameters given in Table I. The next three columns give the contributions of lattice vibrations, intraband free-carrier absorption, and interband free-carrier absorption, respectively, as estimated from Eqs. (19)–(21), and the last column gives the total calculated index.

P [cm^{-3}]	n (Fig. 2)	Δn_{lv}	Δn_{intra}	Δn_{inter}	$n(\text{total})$
1.5×10^{17}	3.5898	−0.00013	−0.00004	−0.00005	3.590
1.1×10^{19}	3.5884	−0.00013	−0.0029	−0.0037	3.582

room temperature. Since this absorption is concentrated at low energies, we find from Eq. (10) that the interband free-carrier contribution to the index of refraction near the absorption edge of p -type GaAs is

$$\Delta n_{inter} \approx -6.3 \times 10^{-22} P / E^2, \quad (21)$$

which exceeds the intraband contributions given in (20), since $n \approx 3.6$.²⁰

We list in Table II the room-temperature index of refraction at 1.37 eV calculated for the two purest samples of Fig. 2, together with the corrections of Eqs. (19)–(21). The validity of the interband free-carrier contribution is sufficiently marginal for the remaining samples of Fig. 2 that we have not included these in Table II. For comparison with the values in Table II we note that the calculated index of refraction in Fig. 1 is 3.585 (this value would not be changed in the third decimal place by the lattice-vibration and free-carrier contributions), and that Marple's²⁰ observed value is 3.588, both at $E = 1.37$ eV and $T = 298^\circ\text{K}$. Although the index differences between samples of different impurity concentrations are quite small, they can be important in the operation of the GaAs injection laser. This is discussed briefly in Sec. V.

The free-carrier contribution to the index of refraction in n -type GaAs can easily be estimated in the same way as for p -type material. If we take the electron effective mass to be $0.072m$, we find

$$\Delta n_{intra} \approx -9.6 \times 10^{-21} N / n E^2, \quad (22)$$

where N is the electron concentration. There is some interband absorption in n -type GaAs,¹⁷ but we find that

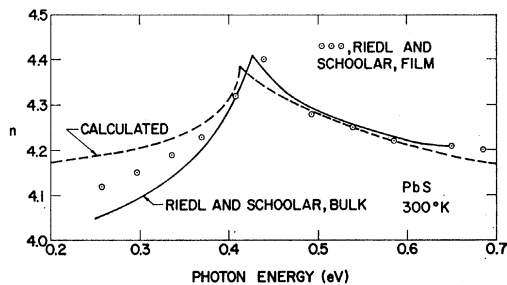


FIG. 3. Index of refraction of PbS at 300°K. The dashed curve is calculated using the parameters listed in Table I. The solid curve is obtained from the bulk reflectivity measurements of Riedl and Schoolar (Ref. 22), with a correction for lattice-vibration and free-carrier effects; the points are obtained from interference measurements on epitaxial films by Riedl and Schoolar, and are uncorrected.

its contribution to the index near the absorption edge is less than 1% of the intraband contribution, and can be neglected.

Lead Sulfide

The room-temperature optical absorption of PbS, PbSe, and PbTe³³ is well represented by the square-root dependence given in Eq. (11). The optical constants above the energy gap have been measured,³⁴ but not to sufficiently high energies that we can determine the characteristic peaks in the imaginary part of the dielectric constant. This uncertainty is not serious for the lead salts, since their optical energy gaps fall at quite a low energy.

The index of refraction of PbS in the range 0.2 to 0.7 eV as calculated from the parameters given in Table I, and the results obtained by reflection on bulk samples and by interference on epitaxially grown film samples by Riedl and Schoolar,²² are shown in Fig. 3. We see that the calculated curve has its peak at too low an energy, and that the height of the calculated peak in the index is too small. The differences may be barely within the experimental errors, since the calculated curve can be lowered by reducing the constant G_1 of Table I. In any case, the calculated and observed values are in good qualitative agreement.

The much bigger peak in the index found in PbS than in GaAs can be ascribed mainly to the smaller energy gap, which leads to a smaller energy denominator in the dispersion integral in Eq. (8). We note that the constant B of Table I, which is $3.44 \times 10^4 \text{ cm}^{-1} \text{ eV}^{-1/2}$ for PbS, is not much different from the corresponding value for GaAs, $4 \times 10^4 \text{ cm}^{-1} \text{ eV}^{-1/2}$, obtained by Kudman and Seidel²⁹ for their purest sample.

The index curves for PbSe and PbTe should look much like the one for PbS, since their optical absorption edges are similar.³³ Preliminary calculations indicate that the index peak, relative to the value of the index at long wavelengths, will be somewhat higher in PbTe than in PbS or PbSe.

Indium Antimonide

Moss, Smith, and Hawkins² noted the relation between the absorption edge and the dispersion of the

³³ W. W. Scanlon, Phys. Chem. Solids **8**, 423 (1959).

³⁴ D. G. Avery, Proc. Phys. Soc. (London) **B66**, 134 (1953); **B67**, 2 (1954). [Note added in proof. See also M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964), where optical constants are deduced for photon energies up to about 15 eV.]

index in InSb. They measured the optical absorption and used their values to calculate the index near the absorption edge. They also measured the index by interference methods. The experiments agree well with the calculated curve, but do not go to high enough values of E to verify the existence of the index peak in the calculated curve. The index peak at the absorption edge, $E \approx 0.18$ eV, is quite clearly seen in the reflectivity data of Morrison.⁵

Zinc Selenide

The optical absorption of ZnSe²⁴ shows a strong peak near 2.8 eV at low temperature, and a rapid rise in absorption, but without a peak, near 2.7 eV at room temperature. The room-temperature reflectivity has a small peak near the absorption edge, but the more pronounced structure that might be expected at low temperatures has apparently not yet been observed.

V. APPLICATION TO INJECTION LASERS

The index of refraction, both in its dependence on wavelength and in its dependence on impurity or carrier concentration, enters in an important way in the theory of the injection laser. The index of the material in that part of the diode where most of the radiative recombination of electrons and holes is taking place, which we call the active region, determines the wavelengths at which the emission peaks of a unit with the Fabry-Perot structure (two flat, parallel faces) will occur either in the high-current region of stimulated emission³⁵ or in the low-current region of spontaneous emission.²¹ This has made possible accurate measurements over a range of wavelengths in the immediate neighborhood of the absorption edge, and we shall compare the results with our calculated values below. The other important bearing of the index of refraction on the operation of an injection laser is its role in the confinement of the emitted radiation to the immediate vicinity of the active region,³⁶⁻³⁸ which strongly affects the losses, and therefore the threshold currents of the most favored modes present in the stimulated emission.

Mode Structure

The emission peaks seen in the radiation emitted along the axis of a Fabry-Perot structure of length L can be described by the equation

$$m\lambda_m = 2nL, \quad (23)$$

where λ_m is the wavelength in vacuum of the m th emission peak, and m is a number which differs by an

integer from one peak to the next. If the mode number is sufficiently large, this leads to

$$\lambda_{m-1} - \lambda_m = \lambda^2 / 2n'L, \quad (24a)$$

where λ is the average of λ_m and λ_{m-1} , and

$$n' = n - \lambda(dn/d\lambda) = n + E(dn/dE). \quad (24b)$$

Nathan, Fowler, and Burns²¹ have analyzed the on-axis spontaneous emission spectrum of a Fabry-Perot diode at 2°K, and have obtained $n'(E)$ for photon energies between 1.42 and 1.48 eV. We have been able to fit their results within 2% with the parameters listed in Table I, and show both the experimental and the calculated curves in Fig. 4. The critical parameters E_i and E_c were obtained by an approximate fit to the experimental data, and the remaining parameters were obtained by a crude extrapolation from the values used for Fig. 1.

The value $E_i = 0.010$ eV which is required to give reasonable agreement with the observed 2°K dispersion curve is much greater than the 0.002–0.003 eV which one would deduce from the absorption data on pure GaAs at very low temperature.²⁶ This larger value reflects the greater tailing of states near the band edges in the impure material in the active region of the GaAs diode than in the relatively pure material used in Sturge's measurements. The discrepancy between the calculated and observed dispersion curves can be reduced if we eliminate the sharp corner present in the model in Eq. (13), which was used for the calculation. This is consistent with the more rounded absorption found in impure p -type samples by Kudman and Seidel²⁹ than in Sturge's measurements. Thus, with a very reasonable model for the absorption edge of the impure material in the active region of a diode, and with no other adjustable parameters, we can obtain excellent agreement with the dispersion of the index observed by Nathan, Fowler, and Burns.²¹

The free-carrier and lattice-vibration contributions

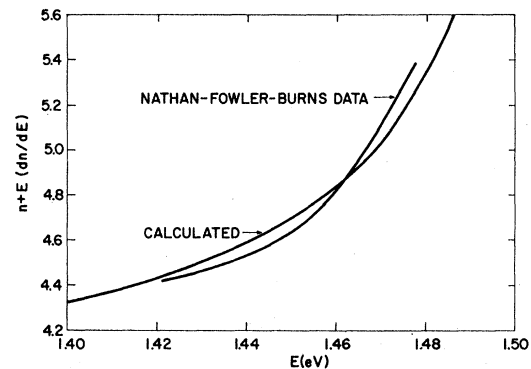


FIG. 4. The quantity $n' = n + E(dn/dE)$ as calculated for GaAs from the parameters listed in Table I, is compared with the values obtained at 2°K by Nathan, Fowler, and Burns (Ref. 21) from interference measurements on spontaneous emission from a Fabry-Perot injection laser.

³⁵ J. D. Kingsley and G. E. Fenner, Bull. Am. Phys. Soc. 8, 87 (1963).

³⁶ A. L. McWhorter, H. J. Zeiger, and B. Lax, J. Appl. Phys. 34, 235 (1963).

³⁷ A. Yariv and R. C. C. Leite, Appl. Phys. Letters 2, 55 and 161 (1963).

³⁸ R. C. C. Leite and A. Yariv, Proc. Inst. Elec. Electron. Engrs. 51, 1035 (1963).

to the index are sufficiently small, and vary sufficiently slowly with photon energy near the absorption edge, that their effect on n' can be ignored. Note that although these terms make a negative contribution to n , they make a positive contribution to n' .

Radiation Confinement

If the index of refraction in the active region of an injection laser is greater than the index of the inactive material on both sides, the effect is like that of a potential well which confines some radiation modes to the neighborhood of the active region.³⁶⁻³⁸ Some confinement will occur even without an index change because of the absorption of light in the inactive region.^{39,40} As the index difference between the active and inactive regions increases, the wave becomes confined more and more to the active region alone, and eventually the power gain per unit length along the junction becomes equal to the gain in the active region. The rather low threshold-current densities that have been observed in GaAs injection lasers suggest that an index change favoring radiation confinement is present.

Three mechanisms have been proposed which can lead to a higher index of refraction in the active region of an injection laser than in the surrounding material. The first is associated with the absorption change due to the population inversion in the active region,^{36,38} the second is the result of higher carrier densities in the inactive region than in the active region,³⁷ and the third is associated with differences in the absorption edge of the active and inactive regions.⁴¹

The free-carrier contribution to the index will help to confine the radiation from an injection laser, at least on the p -type side of the active region, since the hole concentration rises rapidly as one goes into the p -type side of the zinc-diffused GaAs units generally used at present. The situation on the n -type side is less clear, since the active region is thought to lie somewhat on the p -type side of the junction,⁴² so that one would have to compare the free-carrier effects both in the active region and in the adjoining n -type material. Such a comparison requires a specific model of the junction, and will not be attempted here. The approximate index changes associated with free carriers are given in Eqs. (20)–(22). The interband contribution (21) for holes, which is comparable to the intraband contribution, has not been included in previous discussions.

The index change associated with differences in the absorption edge of material in the active and inactive regions of the junction can also affect the radiation confinement. This change can depend quite strongly on wavelength, and can therefore shift the stimulated emission peak somewhat from the position one would

otherwise predict. Unfortunately, the calculation of this index change depends on accurate knowledge of the absorption edge for the material involved in the active and inactive regions of the junction. A number of absorption measurements have been carried out,^{29,43-45} but they either fail to cover the important range of absorption constants between 10^3 and 10^4 cm⁻¹, or are limited to room temperature, or both. Thus, quantitative estimates of this contribution to the index change in the cases of interest for radiation confinement are not possible at present.

The effect of population inversion on the index of refraction can be shown to have the wrong sign for radiation confinement, but may be rather small. The magnitude of the effect is inversely proportional to the thickness of the active region. In the published estimates^{36,38} a thickness of 2×10^{-5} cm has been used, but there are indications that the thickness is larger.⁴²

Since the population inversion reduces the absorption constant near the absorption edge, the index change will be negative, i.e., unfavorable for radiation confinement, on the low-energy side of the maximum absorption change, and positive on the high-energy side. The change in absorption is not given by the same integral over conduction and valence band states as are the spontaneous and the stimulated emission,⁴² and will have the same spectral distribution as the spontaneous emission only at absolute zero, and only if a momentum selection rule applies. Since there is reason to believe that the momentum selection rule will not be valid near the absorption edge of impure material,^{42,46} we expect the peak of the absorption change associated with population inversion to lie at a higher photon energy than does the peak of the spontaneous emission. This will be true even with a selection rule when KT becomes comparable to the spontaneous-emission linewidth. Since the stimulated-emission peak is expected to lie on the low-energy side of the spontaneous-emission peak, except at $T=0$,⁴² we conclude that the index change associated with population inversion will be unfavorable for radiation confinement unless the momentum selection rule is valid and KT is small compared to the spontaneous-emission linewidth.

Nathan, Fowler, and Burns²¹ find at 2°K that the index change with increasing diode current is negative, i.e., unfavorable, or zero in the wavelength range they studied, which included the wavelength of the lasing peak.

Pressure and Temperature Effects

The change in wavelength of a particular mode of a Fabry-Perot structure with temperature is found from

³⁹ G. J. Lasher, IBM J. Res. Develop. **7**, 58 (1963).

⁴⁰ R. N. Hall and D. J. Olechna, J. Appl. Phys. **34**, 2565 (1963).

⁴¹ F. Stern, Bull. Am. Phys. Soc. **8**, 201 (1963).

⁴² G. J. Lasher and F. Stern, Phys. Rev. **133**, A553 (1964).

⁴³ D. E. Hill, Bull. Am. Phys. Soc. **8**, 202 (1963).

⁴⁴ W. J. Turner and W. E. Reese, Bull. Am. Phys. Soc. **8**, 311 (1963); and J. Appl. Phys. **35**, 350 (1964).

⁴⁵ R. Braunstein, J. I. Pankove, and H. Nelson, Appl. Phys. Letters **3**, 31 (1963).

⁴⁶ W. P. Dumke, Phys. Rev. **132**, 1998 (1963).

differentiation of Eq. (23) to be

$$d\lambda/dT = (\lambda/n')[(dn/dT) + (n/L)(dL/dT)], \quad (25)$$

where dn/dT is taken at constant wavelength, and n' is given in (24b). A similar expression holds for pressure changes if T is replaced by p .

Experimental values for most of the quantities in (25) are known, and allow us to deduce the values of dn/dT and dn/dp . We shall consider data at 77°K, for which the emission occurs at about 8390 Å or 1.478 eV.^{47,48} At that temperature, values of $L\delta\lambda/\lambda^2$ of⁴⁹ 0.095 ± 0.005 and⁵⁰ 0.093 ± 0.004 have been reported. Thus, using Eq. (24), we deduce that $n' = 5.3 \pm 0.3$. The index of refraction is approximately 3.58.⁵¹ For the temperature change we can neglect the second term on the right in (25), and find, from $d\lambda/dT = 0.4 \text{ Å}/^\circ\text{K}$,⁴⁸ that $dn/dT = 2.5 \times 10^{-4}/^\circ\text{K}$. For the pressure effect we use $L^{-1}(dL/dp) = -0.42 \times 10^{-6} \text{ cm}^2/\text{kg}$,⁵² and $d\lambda/dp = -0.020 \text{ Å-cm}^2/\text{kg}$,⁴⁷ and find $dn/dp = -1.1 \times 10^{-5} \text{ cm}^2/\text{kg}$.

We shall show in the following section that the temperature and pressure changes of the index of refraction found in this way are quite consistent with our model relating the dispersion of the index near the edge to the rapidly rising absorption there.

VI. EFFECT OF TEMPERATURE AND PRESSURE CHANGES ON THE INDEX OF REFRACTION

The formal treatment we have used, based on Eq. (8), is very easily extended to describe the effect of temperature and pressure changes on the index of refraction provided we know the effect of temperature and pressure on the absorption coefficient and on the other parameters which enter in that equation. It is convenient to consider the absorption edge effects and the effects on the high-energy peaks in the imaginary part of the dielectric constant separately.

At long wavelengths the temperature or pressure dependence of the index of refraction will depend on the changes of the parameters E_j and G_j with temperature and pressure. The changes in E_j can in principle be measured, and some such measurements have been reported.²⁸ On the other hand, the parameter G_j is essentially an empirical parameter, and can best be determined by measurement of the change of the index of refraction with temperature or pressure at photon energies well below the absorption edge.

Temperature or pressure changes generally shift the energy of the absorption edge and change its shape. For a qualitative discussion we shall ignore the change of shape [as characterized, for example, by the parameter B of Eq. (11) or the parameter E_i of Eq. (13)], and shall consider only the temperature or pressure coefficient of the edge. If we further assume that the index can be described as the sum of contributions given in Eqs. (9) and (10), then the temperature or pressure shift of the index will be the sum of a term which depends on the changes in E_j and G_j , and which presumably varies relatively slowly with photon energy, plus another term which depends on changes in E_o or E_c , which will be small at long wavelengths but will be large near the edge.

The main contribution to pressure or temperature changes in the index near the absorption edge is given by the change in the Δn of Eq. (10). If we use the exponential absorption-edge model of Eq. (13), then Δn is given by Eq. (14). We find that when E_c is small, we can to a good approximation write

$$d(\Delta n)/dT = -[d(\Delta n)/dE](dE_c/dT), \quad (26)$$

with an analogous equation for pressure changes. A similar result would follow from Eq. (12) if we replace E_c by E_g .

To take into account the effect of temperature or pressure on the slowly varying contribution to the index we shall add to (26) the temperature dependence of the index at long wavelengths, where the main effect arises from the variation of E_j and G_j . The sum of these two terms should give a rough estimate, good to perhaps 20%, for the variation of the index near the absorption edge with temperature or pressure.

We use GaAs for a numerical example, and deduce from the values $n = 3.58$ and $n' = 5.3$ which we used in the previous section that $dn/dE = 1.2 \text{ eV}^{-1}$ near $E = 1.478 \text{ eV}$, which is the emission peak at 77°K for the GaAs injection lasers used in the pressure and temperature measurements^{47,48} described in the previous section. Our calculations show that about one-third of this dispersion arises from the high-energy contribution to the index, as given in (9), and that the remainder is the contribution of the edge. Thus we estimate that $d(\Delta n)/dE \approx 0.8 \text{ eV}^{-1}$.

Numerical estimates of the temperature dependence of the index at 77°K are complicated by the fact that the energy gap and other quantities do not vary linearly with temperature at low temperatures. From Sturge's data²⁶ we can deduce the temperature coefficient of the energy gap to be $-2 \times 10^{-4} \text{ eV}/^\circ\text{K}$ near 77°K. This leads via Eq. (26), to $d(\Delta n)/dT \approx 1.6 \times 10^{-4}/^\circ\text{K}$. The temperature dependence of the index at long wavelengths is $dn/dT = 1.5 \times 10^{-4}/^\circ\text{K}$,⁵³ but this is the value determined between 100 and 400°K,

⁴⁷ M. J. Stevenson, J. D. Axe, and J. R. Lankard, IBM J. Res. Develop. **7**, 155 (1963); see also G. E. Fenner, J. Appl. Phys. **34**, 2955 (1963) and Ref. 54.

⁴⁸ G. Burns and M. I. Nathan, Proc. Inst. Elec. Electron. Engrs. **51**, 471 (1963). Temperature shifts below 77°K have been measured and discussed by W. E. Engeler and M. Garfinkel, J. Appl. Phys. **34**, 2746 (1963).

⁴⁹ Quoted in the talk by J. D. Kingsley and G. E. Fenner (Ref. 35).

⁵⁰ G. Burns, F. H. Dill, Jr., and M. I. Nathan, Proc. Inst. Elec. Electron. Engrs. **51**, 947 (1963).

⁵¹ D. T. F. Marple (unpublished), quoted in the talk by J. D. Kingsley and G. E. Fenner (Ref. 35).

⁵² C. W. Garland and K. C. Park, J. Appl. Phys. **33**, 759 (1962).

⁵³ M. Cardona, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovakian Academy of Sciences, Prague, 1961), p. 388.

and is likely to overestimate the effect at 77°K. The sum of the two contributions to the temperature dependence of the index gives an estimate of $3.1 \times 10^{-4}/^\circ\text{K}$ or less, which is to be compared with the value $2.5 \times 10^{-4}/^\circ\text{K}$ deduced from diode measurements and mentioned in the previous section.

For the pressure case we use $dE_g/dp = 1.13 \times 10^{-5}$ eV/bar for GaAs at 77°K, as measured from the shift of the spontaneous emission peak with pressure,⁵⁴ and find from the pressure analog of (26) that $d(\Delta n)/dp \approx -9 \times 10^{-6}/\text{bar}$. The long-wavelength pressure dependence of the index of refractions is not known at 77°K, but if we use the room temperature value $-2.3 \times 10^{-6}/\text{bar}$,⁵⁵ we find the estimated pressure shift of the index of refraction of GaAs at 8390 Å to be $-1.1 \times 10^{-5}/\text{bar}$, in essential agreement with the value deduced from diode measurements.

We conclude that our model can account at least qualitatively, and in some cases quantitatively, for the dispersion of the index of refraction near the absorption edge of GaAs and other semiconductors and for its change with temperature and pressure.

ACKNOWLEDGMENTS

I am indebted to J. D. Axe, G. Burns, J. R. Dixon, A. B. Fowler, R. W. Keyes, G. J. Lasher, M. I. Nathan, W. E. Reese, and W. J. Turner for profitable discussions of this work and the related experiments, to H. R. Riedl and R. B. Schoolar for making available their experimental results on PbS prior to publication and for valuable discussions, and to D. T. F. Marple for making available unpublished measurements of the index of refraction of GaAs and for permission to quote the results here.

APPENDIX: EVALUATION OF THE DISPERSION INTEGRAL

In the numerical calculations for the index of refraction $n(E)$ using Eq. (8) it is convenient to take a common grid of points for both E and E' , the latter being the variable over which the integration is carried out. Since the integrand of the dispersion integral is most rapidly varying near the absorption edge, and the structure in the index is most pronounced there, a finer

grid is taken near the edge. This, however, leads to irregularities in $n(E)$ if a simple trapezoidal rule is used for the numerical integration near a change in the grid interval.

To find the reason for the error, we compare the results of an exact integration of the dispersion integral over a small energy interval near $E' = E$ with the corresponding expression given by the trapezoidal rule. For this purpose we replace the numerator in the dispersion integral by a linear expression $A + BE'$. The exact integration gives

$$P \int_{E+\delta_1}^{E+\delta_2} (A + BE')(E'^2 - E^2)^{-1} dE' = \frac{A + BE}{2E} \ln \left| \frac{\delta_2}{\delta_1} \right| + \frac{BE - A}{2E} \ln \left(\frac{2E + \delta_2}{2E + \delta_1} \right), \quad (\text{A1})$$

where P means that the principal value has been taken, and neither δ_1 nor δ_2 can vanish. Trapezoidal rule integration gives, to first order in δ/E ,

$$\frac{A + BE}{2E} \frac{\delta_2^2 - \delta_1^2}{2\delta_1\delta_2} + \frac{BE - A}{2E} \frac{\delta_2 - \delta_1}{2E}. \quad (\text{A2})$$

When δ_1 and δ_2 are small compared to E , which we shall assume throughout this discussion, the second term of (A2) agrees with the second term of (A1) to first order in δ/E . For equal intervals straddling the point $E' = E$, i.e., for $\delta_1 = -\delta_2$, the first terms of both (A1) and (A2) will vanish. But if unequal intervals are taken, the first term in the trapezoidal rule can differ substantially from the first term of the exact integration, and will have the wrong sign when $\delta_1\delta_2 < 0$.

To avoid the errors introduced by trapezoidal rule integration near a change in the integration interval, we used Eq. (A1) in our calculations instead of the trapezoidal rule whenever

$$|\delta_1\delta_2| \leq 0.4(\delta_1^2 + \delta_2^2), \quad (\text{A3})$$

retaining only terms to second order in δ/E in the expansion of the logarithm in the second term of (A1). With this procedure the numerical results for $n(E)$ were found to be independent of the position of a change in the integration interval to six significant figures. A run with about 170 grid points and three iterations of Eq. (8) required about 40 seconds of computing time on the IBM 7094 Data Processing System.

⁵⁴ J. Feinleib, S. Groves, W. Paul, and R. Zallen, Phys. Rev. **131**, 2070 (1963). We are indebted to Professor Paul for making a copy of this paper available.

⁵⁵ M. DeMeis and W. Paul (unpublished), quoted in Ref. 54.