Franz-Keldysh Effect of the Refractive Index in Semiconductors

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Changes in the shape of the fundamental absorption edge of a semiconductor as induced by strong electric fields will lead to correlated changes in the refractive index. Computation of the dispersion integral for an absorption edge that is modified by the Franz-Keldysh effect proves that the refractive index of germanium and gallium arsenide changes by as much as 0.02, for instance, for electric fields characteristically present in a *p-n* junction. The fact that the refractive index depends upon electric fields extends the Franz-Keldysh effect to reflection phenomena, even if this refractive index is much greater than the extinction coefficient, which is usually the case near the fundamental edge of semiconductors. Based on this dependence of the refractive index upon electric fields, the field effect of the reflectance in germanium is interpreted and good agreement is obtained with experiment. It is pointed out that this mechanism could be relevant for the confinement of the radiation in a gallium arsenide laser.

I. INTRODUCTION

NUMEROUS experimental observations have confirmed the prediction of Franz[1] and Keldysh[2] that in the presence of an electric field the fundamental absorption edge of semiconductors acquires an exponential tail,[3–6] which is sometimes referred to as a shift of the edge towards lower photon energies. Although it is generally recognized that as a result of this effect the transmission properties of semiconductors in the vicinity of their fundamental edge depend upon electric fields, very little attention has been paid to the influence on the reflectance. Since in this wavelength region the extinction coefficient is always much smaller than the refractive index, the reflectance is almost entirely determined by the latter. It can easily be shown that the field-induced change in the extinction coefficient alone changes the reflectance only by amounts beyond detection.

This argument, however, neglects the close relation between the two optical constants as described by the dispersion relation.[7,8] A change in the absorption coefficient due to Franz-Keldysh effect cannot be without consequence to the refractive index. If the correlated change is sufficiently large, the whole complex of reflection phenomena—on external as well as on internal interfaces—becomes dependent upon electric fields in about the same manner the Franz-Keldysh effect acts on the transmission properties.

In this paper, calculations are presented of the refractive index of germanium and gallium arsenide in the presence of electric fields. In the wavelength region of the fundamental edge the field-induced change in the absorption coefficient is computed using expressions which Callaway[9] and Tharmalingam[10] derived. Application of the Kramers-Kronig dispersion integral to this change produces the correlated change in the refractive index.

Based on these numerical results, an interpretation of the field effect of the reflectance in germanium is presented. It was recently reported[11–14] that the reflectance near photon energies of direct interband transitions depends upon the surface potential at the reflecting interface. Good agreement is obtained with this experimental observation assuming a Franz-Keldysh effect of the refractive index in the strong electric fields of the surface potential barrier. The explanation falls short of the experiment by two orders of magnitude, if only the absorption coefficient is assumed to change.

Considering reflection from internal interfaces, it is pointed out that the Franz-Keldysh effect of the refractive index may be relevant to radiation confinement in narrow *p-n* junctions.

II. THE REFRACTIVE INDEX IN AN ELECTRIC FIELD

1. Field-Induced Change in the Absorption Coefficient

The basic studies of the influence of an electric field on the optical absorption edge of semiconductors were done by Franz[1] and Keldysh.[2] Their results were extended to photon energies greater than the band gap by

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[2] W. L. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 1138 (1958) [English transl.: Soviet Phys.—JETP **7**, 788 (1958)].
[3] A. Frova and P. Handler, *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 157.
[4] M. Chester and P. H. Wendland, Phys. Rev. Letters **13**, 193 (1964).
[5] T. S. Moss, J. Appl. Phys. **32**, 2136 (1961); L. M. Lambert, Bull. Am. Phys. Soc. **9**, 619 (1964).
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[7] F. Stern, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 327.
[8] F. Stern, Phys. Rev. **133**, A1653 (1964).
[9] J. Callaway, Phys. Rev. **130**, 549 (1963); *ibid.* **134**, A998 (1964).
[10] K. Tharmalingam, Phys. Rev. **130**, 2204 (1963).
[11] B. O. Seraphin, *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 165.
[12] B. O. Seraphin, R. B. Hess, and N. Bottka, Bull. Am. Phys. Soc. **9**, 714 (1964).
[13] B. O. Seraphin, R. B. Hess, and N. Bottka, J. Appl. Phys. **36**, 2242 (1965).
[14] B. O. Seraphin and R. B. Hess, Phys. Rev. Letters **14**, 138 (1965).

Bulyanitsa,[15] Callaway,[9] and Tharmalingam.[10] They obtained explicit expressions for the absorption coefficient which can readily be evaluated. For the purpose of this paper is it sufficient to use the weak-field approximation for the absorption coefficient $\alpha(\omega,F)$ in the presence of an electric field F, as derived by Tharmalingam:

$$\alpha(\omega,F)=(C\theta_F^{1/2}/\omega)[|d\,\mathrm{Ai}(\beta)/d\beta|^2-\beta|\mathrm{Ai}(\beta)|^2], \quad (1)$$

with $\theta_F^3=(e^2F^2/2\mu\hbar)$ and $\beta=(\omega_1-\omega/\theta_F)$. Here $\mathrm{Ai}(\beta)$ is the Airy function,[16] defined by

$$\mathrm{Ai}(\beta)=\frac{1}{\sqrt{\pi}}\int_0^\infty \cos(\tfrac{1}{3}u^3+u\beta)du. \quad (2)$$

e and $\hbar$ are the charge of the electron and Planck's constant, respectively. $\hbar\omega_1$ is the energy of the band gap. μ is the reduced mass of the electron-hole pair. In the following calculations, $\mu=0.069m_0$ for germanium[17] and $\mu=0.065m_0$ for gallium arsenide[18] are used. C is a constant involving the matrix elements between the periodic parts of the Bloch states at the band edges, in addition to material parameters and fundamental constants. C will not be given explicitly, since no calculation of the absorption coefficient from first principles is intended. C and ω_1 will rather be used as free parameters in order to fit the limiting case of Eq. (1) for $F\to 0$ to measured values of the absorption coefficient. For $F\to 0$, Eq. (1) goes over into the familiar expression for the absorption due to direct allowed transitions behind the edge[19] $(\omega>\omega_1)$

$$\alpha(\omega,0)\to 0.3187(C/\omega)(\omega-\omega_1)^{1/2} \quad (3)$$

and gives $\alpha\to 0$ as $F\to 0$ in front of the edge $(\omega<\omega_1)$. C and ω_1 are adjusted such that Eq. (3) reproduces as close as possible the upper part of the experimental absorption edge. $C=7.75\times10^{11}$ cm^{-1} sec$^{-1/2}$, $\omega_1=1.22\times10^{15}$ sec^{-1} give the best fit for the measurement of Dash and Newman[20] of the absorption edge in germanium, and $C=1.76\times10^{12}$ cm^{-1} sec$^{-1/2}$, $\omega_1=2.15\times10^{15}$ sec^{-1} reproduce the values of Moss[18] for gallium arsenide satisfactorily. Using these values, the change $\Delta\alpha(\omega,F)$

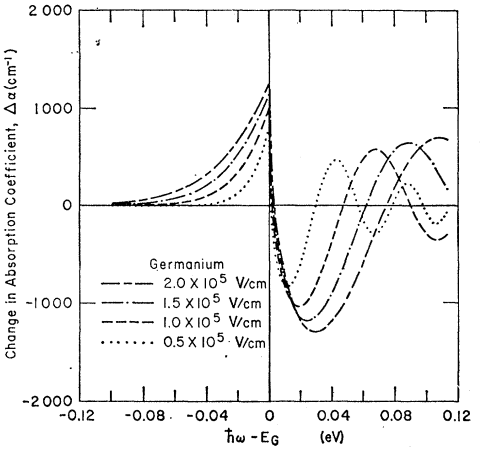

FIG. 1. The change in the absorption coefficient of germanium, as induced by electric fields of different strength, calculated from Eq. (4).

$=\alpha(\omega,F)-\alpha(\omega,0)$ is calculated by subtracting Eq. (3) from Eq. (1).

$$\Delta\alpha(\omega,F)=\frac{C}{\omega}\left\{\theta_F^{1/2}\left[\left|\frac{d\,\mathrm{Ai}(\beta)}{d\beta}\right|^2-\beta|\mathrm{Ai}(\beta)|^2\right]-0.3187(\omega-\omega_1)^{1/2}\right\}, \quad (\omega>\omega_1) \quad (4)$$

$$=\frac{C}{\omega}\theta_F^{1/2}\left[\left|\frac{d\,\mathrm{Ai}(\beta)}{d\beta}\right|^2-\beta|\mathrm{Ai}(\beta)|\right], \quad (\omega<\omega_1).$$

Plots of the numerical values of $\Delta\alpha$ versus photon energy as obtained from Eq. (4) are shown in Figs. 1 and 2 for germanium and gallium arsenide, respectively. The calculations on either side of the funda-

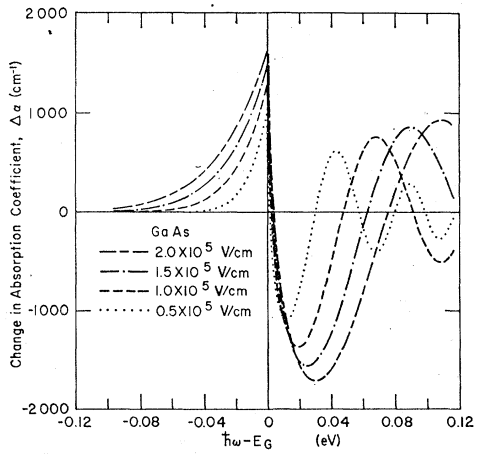

FIG. 2. The change in the absorption coefficient of gallium arsenide, as induced by electric fields of different strength, calculated from Eq. (4).

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[16] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 519.

[17] T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications, Ltd., London, 1959), p. 132. Correctly, a frequency-dependent reduced mass $\mu(\omega)$ should be used instead of this average value for the minima in the (111)-direction. This simplification does not affect the calculations seriously. Considering the light holes or using the electron mass for the direct transition, for instance, would only result in a slight compression of the horizontal scale towards the center of Fig. 1–4.

[18] T. S. Moss, J. Appl. Phys. **32**, 2136 (1961).

[19] J. Bardeen, F. J. Blatt, and L. H. Hall, *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p.146.

[20] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

mental absorption edge were performed for four values of the electric field.

The plots are similar for both materials. The exponential tail in front of the edge, which is experimentally confirmed in germanium[3] as well as in gallium arsenide,[5] is followed by damped oscillations of $\Delta\alpha$ behind the edge. Amplitude, interval of periodicity and damping length increase with increasing electric field. In the weak-field approximation used here these oscillations simply reflect the properties of the Airy function in Eq. (1).

2. The Dispersion Relation

The refractive index n is coupled to the absorption coefficient α by the Kramers-Kronig dispersion relation[7,8]

$$n(\omega,0)-1=\frac{c}{\pi}\int_0^\infty \frac{\alpha(\omega',0)}{\omega'^2-\omega^2}d\omega'. \quad (5)$$

If an electric field F changes $\alpha(\omega',0)$ to $\alpha(\omega',F)=\alpha(\omega',0)+\Delta\alpha(\omega',F)$, Eq. (5) can be written

$$n(\omega,F)-1=\frac{c}{\pi}\int_0^\infty \frac{\alpha(\omega',0)}{\omega'^2-\omega^2}d\omega'+\frac{c}{\pi}\int_0^\infty \frac{\Delta\alpha(\omega',F)}{\omega'^2-\omega^2}d\omega'. \quad (6)$$

Subtracting Eq. (5) from Eq. (6) gives the change Δn in the refractive index, produced by the presence of the electric field

$$\Delta n(\omega,F)=n(\omega,F)-n(\omega,0)=\frac{c}{\pi}\int_0^\infty \frac{\Delta\alpha(\omega',F)}{\omega'^2-\omega^2}d\omega'. \quad (7)$$

In principle, all the wavelength regions in which the electric field induces a Franz-Keldysh effect of the absorption coefficient, contribute to the integral in Eq. (7). In most cases, however, the onset of the next higher interband transition will be too far away on the wavelength scale to make a noticeable contribution to Eq. (7). It is proved in the Appendix for the case of germanium, for which experimental results on the Franz-Keldysh effect above the fundamental edge are available,[14] that only the region around this edge needs to be considered.

Plots for the numerical values of Δn versus photon energy as obtained from Eq. (7) are shown in Figs. 3 and 4 for germanium and gallium arsenide, respectively. Electric fields and range of photon energies around the absorption edge are identical with Figs. 1 and 2, from which the respective values for $\Delta\alpha$ were obtained. The details of the numerical calculation are given in the Appendix. The diagrams demonstrate to what extent the refractive index is affected by electric fields of up to 2×10^5 V/cm. In front of the edge, the index increases by amounts of the order of 10^{-3}, with the peak of the increase moving away from the edge for increasing fields. A steep drop of Δn to negative values of up to 2×10^{-2} follows right at the photon energy of the band gap. Δn penetrates behind the edge in damped oscillations as a consequence of the similar oscillations of $\Delta\alpha$, the change in the absorption coefficient.

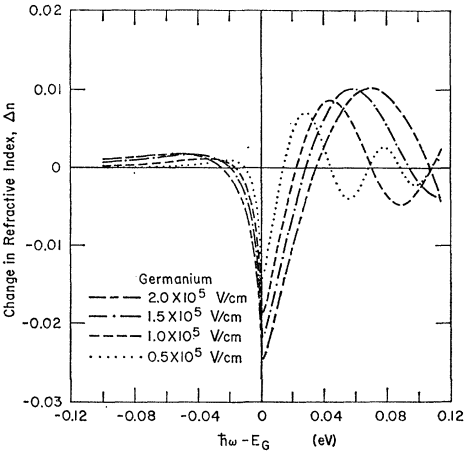

FIG. 3. The change in the refractive index of germanium, as induced by electric fields of different strength, calculated from Eqs. (7) and (4).

III. APPLICATIONS

1. Field Effect of the Reflectance in Germanium

It was recently reported[11–14] that the reflectance of germanium near photon energies of direct interband transitions depends upon the surface potential at the reflecting surface and can therefore be modulated by application of a transverse electric field. For the direction of the modulating field which builds up the surface potential barrier further, the reflectance R dropped by amounts of typically $\Delta R/R\approx10^{-3}$. The peak of this negative response, which is located at the photon energy of the correlated absorption edge, is sometimes accompanied by one or two peaks of positive response,

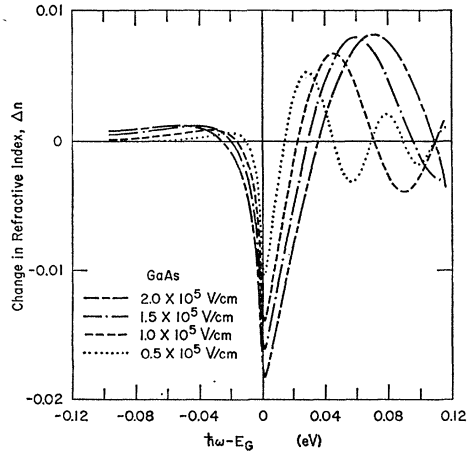

FIG. 4. The change in the refractive index of gallium arsenide, as induced by electric fields of different strength, calculated from Eqs. (7) and (4).

one on either side. The effect was studied in particular as a function of the surface conditions for the fundamental absorption edge at 0.80 eV. It was found that the response is always negative regardless of the direction into which the potential barrier grows and further, that the effect disappears for the flat-band position in which no potential barrier exists at the interface. It was concluded from these two observations that the electric field in the potential barrier, rather than the external modulation field, is the cause of the change in reflectance. An attempt to support this conclusion by a numerical estimate fails, however, as long as only the usual Franz-Keldysh effect of the absorption coefficient is assumed. The total differential of

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{8}$$

with respect to the two optical constant n and k gives for the fundamental absorption edge of germanium, using $n=4.00$ and $k=1.55\times10^{-2}$,

$$\Delta R/R=0.267\Delta n+0.0022\Delta k\,, \tag{9}$$

where

$$\Delta k=(\lambda/4\pi)\Delta\alpha. \tag{10}$$

Transmission measurements through reverse-biased p-n junctions show that a peak value for $\Delta\alpha$ of less than 10^3 cm^{-1} is obtained for a field strength of 0.5×10^5 V/cm.[3] Using this value of $\Delta\alpha<10^3$ cm^{-1} in Eq. (10) and inserting the resulting Δk value in Eq. (9) produces $\Delta R/R<2\times10^{-5}$, in disagreement with the experimental value of 10^{-3} by almost two orders of magnitude.

If, on the other hand, the field-induced change in the refractive index is calculated by inserting the $\Delta\alpha$ function for the same field strength into the dispersion integral Eq. (7), it is easily seen from Fig. 3 that the Δn values of approximately 10^{-2} bring Eq. (9) into the right order of magnitude. We conclude, therefore, that even on this very general basis it is necessary to assume the coupling of n and k, as described by Eq. (7), in order to obtain agreement with the experiment as to the order of magnitude. The agreement goes much further than this, however. In a previous paper[13] it was shown that by inserting experimental $\Delta\alpha$ values into Eq. (7) for fields determined from field effect measurements, the spectral distribution of the effect could be satisfactorily reproduced in front of the edge. This can be demonstrated easily from Fig. 3 as well. Since $\Delta R/R$ is essentially a linear function of Δn, according to Eq. (9), it follows the Δn plot of Fig. 3. A negative center peak at the edge is accompanied on either side by a positive satellite peak. Further oscillations of the effect on the short-wavelength side of the edge are rapidly damped for these small fields. [*Note added in proof.* J. C. Phillips (private communication) points out that lifetime broadening presumably rounds off the sharp corners at $E=E_G$ and damps the oscillations more rapidly.] That it is necessary to assume at least one of these oscillations, however, in order to reproduce the almost always observed peak behind the edge, proves in our opinion that these oscillations are real. Transmission measurements of the Franz-Keldysh effect, restricted to the regions of smaller absorption in front of the edge, were not able to prove these oscillations so far.

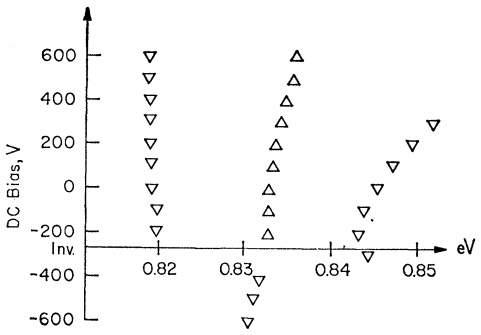

FIG. 5. Wavelength position of the peak reflectance response of a germanium surface at −65°C as caused by an alternating electric field perpendicular to this surface. Different dc bias superimposed on the ac field represent different surface conditions, with the inversion point from p- to n-type surface coinciding with the abscissa.

Figures 5 and 6 demonstrate that the wavelength positions of these peaks as well as the phase relation between reflectance response and modulating field are reproduced correctly by Eqs. (7) and (9). Figure 5 is repeated from Ref. 13 and shows how the three peaks move on the wavelength scale if a dc bias increases the height of the potential barrier, around which the ac field of constant amplitude modulates the surface potential and therefore the reflectance. With −260 V producing the field-free flat-band position, according to

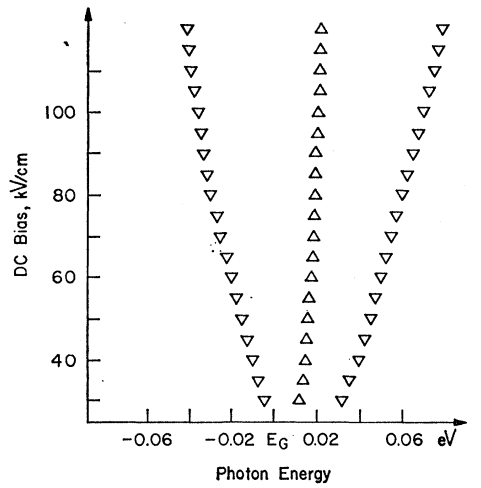

FIG. 6. Simulation of the experimental situation of Fig. 5 by assuming a variable dc bias superimposed on an ac field of constant amplitude in Eqs. (7) and (9). Orientation of the triangles in both figures signifies the phase relation between reflectance response and modulating field.

simultaneous field-effect measurement, triangles above the abscissa belong to an n-type surface of increasing average field strength in the potential barrier. Triangles with the base up represent a positive peak of $\Delta R/R$ produced by the positive half-wave of the modulating field, and triangles base down mean that $\Delta R/R$ goes negative when the positive half-wave increases the field strength in this n-type surface.

Figure 6 plots the results of a calculation which simulates the experiment by superimposing a modulation field of 10^4 V/cm constant amplitude onto a dc bias field of variable strength. The wavelength position of the first three peaks of $\Delta R/R$ is plotted as a function of this dc bias. They show the correct phase relation to the modulating field, as indicated by the orientation of the triangles. In addition to this, the peaks move into the right direction if the average field strength is increased. The short-wavelength peak moves stronger to higher energies than the center peak does and the long-wavelength peak moves slightly to smaller energies. Since the measurement was taken at -65°C, the position of the peaks in relation to the edge is approximately correct, the energy gap being 0.833 eV at this temperature. Since the experimental peaks fit into Fig. 6 in the lowest part, up to 20 kV/cm only, the separation of the peaks by about 0.01 eV agrees well in both cases.

It is concluded that not even on the very general basis of Eqs. (8) and (9) can an explanation be given for the field effect of the reflectance in germanium, if only the absorption coefficient is assumed to change in the electric field. But that agreement is found on a large scale if the refractive index is assumed to be affected, too, according to the dispersion relation of Eq. (7).

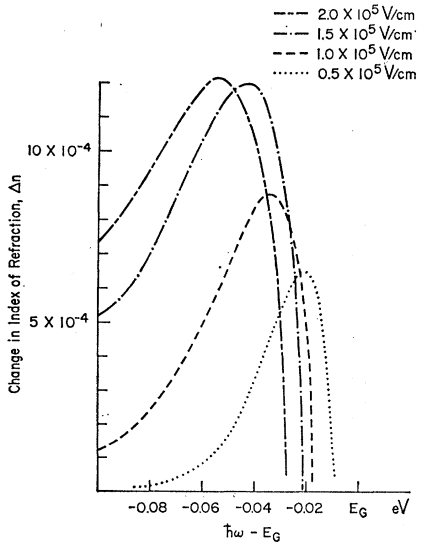

FIG. 7. The change in the refractive index of gallium arsenide, as induced by electric fields of different strength. Enlarged detail of Fig. 4 for photon energies smaller than the gap.

2. Radiation Confinement in Narrow p-n Junctions

Figure 7 presents an enlarged detail of Fig. 4 for photon energies smaller than the fundamental absorption edge. The electric fields for which Δn is plotted, typical for unbiased narrow p-n junctions, raise the refractive index by amounts of up to 1.2×10^{-3}. The peak of this increase shifts towards the edge E_G for decreasing electric field, reducing "linewidth" and height at the same time. The peak moves away from the edge for increasing field, leveling off in height, but spreading out in width. In a previous paper,[21] the wavelength position of the peak increase was expressed in terms of the forward bias and the built-in potential of a linear-gradient-type junction. It was pointed out that this mechanism contributes in principle to the radiation confinement in a gallium-arsenide injection laser, but that no final conclusion can be drawn at the present time as to the extent of this contribution.

IV. SUMMARY

Relatively large changes in the refractive index of a semiconductor of up to 0.02 must be expected if the fundamental absorption edge is modified by the presence of an electric field. The change is sufficiently large to produce Franz-Keldysh–type effects for this wavelength region not only in transmission, but also in reflection.

The calculations are applied to the recently reported field effect of the reflectance in germanium. The Franz-Keldysh effect of the absorption coefficient alone falls short of the experiment by two orders of magnitude. However, the concept of a field-dependent index of refraction, as developed by these calculations, satisfactorily reproduces the experimental results as to sign, magnitude, spectral distribution, and shift of the peaks with increasing field.

APPENDIX

The dispersion integral in Eq. (7) was calculated on the IBM 7094 Data Processing System, using Simpson's rule over a grid size of $\Delta\omega=1\times10^{12}$ sec^{-1}. This grid separates the points equidistantly by 4.13×10^{-3} eV on the abscissa of Figs. 1–4, sufficiently close to each other even for the region around the pole $\omega'=\omega$ of the integrand in Eq. (7). Since $\Delta n(\omega)$ was computed for grid points only, two regular grid intervals $\Delta\omega$ straddled the pole $\omega'=\omega$, contributing the principal value of the integral

$$P\int_{\omega-\Delta\omega}^{\omega+\Delta\omega}\frac{d\omega'}{\omega'^2-\omega^2}=-\frac{1}{2\omega}\ln\left|\frac{2\omega+\Delta\omega}{2\omega-\Delta\omega}\right|. \qquad \text{(A1)}$$

Equation (7) calls for integration over the whole frequency range $0<\omega'<\infty$. Fortunately, the integrand converges so rapidly that in order to calculate $\Delta n(\omega)$

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over 0.12 eV on either side of the edge E_G, the integration had to be carried out over an interval A-B, only slightly larger than the range of Δn. A and B are determined from the requirement that the total contribution from regions outside A-B should not exceed 1% of the integral over A-B

$$\int_0^A \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2}+\int_B^\infty \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2} \leq 0.01\int_A^B \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2}, \quad \text{(A2)}$$

even for $\hbar\omega=E_G\pm 0.12$ eV. Calculations show that $A=E_G-0.125$ eV, and $B=E_G+0.30$ eV, satisfy the inequality of Eq. (A2).

Aside from this question of convergence, an estimate must be made for the contributions from interband transitions above the fundamental edge. The next reflectance response comparable in strength to the response at 0.8 eV was observed in germanium at 2.11 eV. Approximating this response by assuming a constant $\Delta\alpha=5\times10^2$ cm^{-1} between the photon energies $E_1=2.05$ eV and $E_2=2.15$ eV, an upper limit for the contribution δn of this transition to the refractive index at the high-energy end $E_0=E_G+0.12$ eV is obtained by

$$\delta n(E_0)=\Delta\alpha\frac{\hbar c}{\pi}\int_{E_1}^{E_2}\frac{dE'}{E'^2-E_0^2}<\Delta\alpha\frac{\hbar c}{\pi} \times\frac{(E_2-E_1)}{E_1^2-E_0^2}=9.4\times10^{-5}. \quad \text{(A3)}$$

This proves that even the closest transition of considerable response contributes only amounts of the order of 1% to the Δn in the region of the fundamental edge.

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Photoemission Investigation of the Band Structure of PbTe†

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Measurements of the spectral distribution of photoemissive quantum yield and the energy distribution of photoemitted electrons from PbTe for 5.0 eV $<h\nu<$ 11.5 eV are reported. The electron affinity is found to be 4.6±0.3 eV. Regions with high density of states are located 0.7 and 1.2 eV below the valence-band maximum and assigned to the (L_4^+,L_5^+) and L_6^+ symmetry points, respectively. By using the photoemission data and Cardona and Greenaway's optical data, the L_6^- and (L_5^-,L_4') conduction-band points are located approximately 1.3 eV above the valence-band maximum. A high-density point is found 2.4 eV below the valence-band maximum. Evidence is presented that this high-density point is not due solely to structure near the L point.

I. INTRODUCTION

In recent years there has been considerable interest in the band structure of PbTe and the other lead salts. First-principle theoretical calculations have proved difficult because of problems in determining both the core and valence potentials. However, the recent work of Pratt and Ferreira and of Conklin, Johnson, and Pratt, which uses only a minimum of experimental data, has produced reasonable results at the L point.[1]

By making use of the Shubnikov–de Haas method, and other experimental data, the band structure has been determined in detail at the band extrema which are located at the L point.[2,3] Through consideration of the interactions with other bands at the L point necessary to give the observed band structure, Cuff *et al.*[4] have estimated the location of the other bands near the L-point extrema. Kleinman and Lin[5] have used the data at the extrema as well as the optical data of Cardona and Greenaway[6] as the basis for a pseudopotential band calculation.

The only experimental studies previously available which gave direct information concerning the band structure away from the extrema are contained in the optical studies of Cardona and Greenaway.[6] These

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