TABLE I. Approximate concentrations and transition temperatures.

Acceptor	N_A in acc/cc	T_c in °K
B	10^{18}	0.06
Al	3×10^{18}	0.17
Ga	4×10^{18}	0.22
In	10^{20}	5.6

at very high concentrations, the acceptor states gain more energy by binding into hydrogen-like molecules and finally bands than they gain due to the Jahn-Teller effect. The energy of binding into hydrogen-like molecules comes from both direct Coulomb and exchange interactions. For concentrations in the range of interest, this binding energy is much larger than the energy due to Van der Waals forces between acceptor states and the direct magnetic coupling between acceptor states.

Therefore, one must know at what concentration the molecular binding energy exceeds the energy lowering computed from (9). Table I gives the approximate concentrations at which this occurs, and the transition temperatures associated with these concentrations.

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Band Structure of Gallium Phosphide from Optical Experiments at High Pressure[*]

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The effect of hydrostatic pressure on the following optical properties of GaP has been measured at room temperature: the fundamental absorption edge region from 2.2 to 2.7 eV, an infrared absorption band appearing in n-type material at 0.3–0.5 eV, peaks in the reflectivity spectrum at 2.8 and 3.7 eV, and recombination radiation in forward-biased p-n junctions at 1.7–2.3 eV. The results have been interpreted by means of a proposed energy band structure in which the conduction band states X_1^c, X_3^c, Γ_1^c, Γ_{15}^c are located at energies of 2.2, 2.5, 2.8, 3.7 eV, respectively, above the valence band maximum at Γ_{15}^v. The following pressure coefficients have been measured (the transition involved is given in parenthesis), where energy is expressed in eV and pressure in 10^6 bars: $E_G(\Gamma_{15}^v \rightarrow X_1^c)=2.22-1.1P$; $E_0(\Gamma_{15}^v \rightarrow \Gamma_1^c)=2.78+10.7P$; $E_0'(\Gamma_{15}^v \rightarrow \Gamma_{15}^c)=3.71+5.8P$; $\Delta E_2(X_1^c \rightarrow X_3^c)=0.3+1P$. The coefficients of E_G and E_0' are close to those for the corresponding transitions in Si; that of E_0 is close to the corresponding coefficient in Ge. The weak reflectivity peak at 2.8 eV, the direct gap, shifts with temperature at a rate of about -4.6×10^{-4} eV/°K, compared to a value of about -5.2×10^{-4} eV/°K for the 2.2 eV indirect gap.

1. INTRODUCTION

THIS paper describes an experimental investigation of the electronic energy band structure of GaP. The approach taken in this study was to measure the effect of hydrostatic pressure on certain optical properties in the infrared, visible, and near ultraviolet regions of the spectrum. Included in these were absorption near the fundamental absorption edge, extrinsic absorption, reflectivity, and recombination radiation. Several features of the lowest conduction bands have been elucidated in the energy range from 2 to 4 eV above the valence band maximum.

Part of the basis for this work is a systematic correlation inferred from earlier work on pressure effects in group 4 and group 3–5 semiconductors.[1–8] It has been observed that corresponding energy separations in these materials have similar pressure coefficients. In other words, the effect of pressure on the energy of an electronic transition depends primarily on the particular type of final and initial states involved (each specified by a band index n, a reduced wave vector k, and a group-theoretic classification), and is relatively insensitive to choice of material from among this class of simple semiconductors. We have listed some pressure

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[*] Research supported by the U. S. Navy Office of Naval Research.

[1] Some of the principal results of this work were briefly mentioned in R. Zallen and W. Paul, Bull. Am. Phys. Soc. **9**, 61 (1964).

[2] W. Paul and D. M. Warschauer, Phys. Chem. Solids **5**, 89 (1958); **5**, 102 (1958); **6**, 6 (1958).

[3] W. Paul, Phys. Chem. Solids **8**, 196 (1959).

[4] W. Paul, J. Appl. Phys. **32**, 2082 (1961).

[5] W. Paul and D. M. Warschauer, *Solids under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963), Table 8-4, p. 226.

[6] W. Paul and H. Brooks, Progr. Semiconductors **7**, 135 (1963).

[7] R. Zallen, W. Paul, and J. Tauc, Bull. Am. Phys. Soc. **7**, 185 (1962); some of these data are shown in the article by J. Tauc, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (Institute of Physics and the Physical Society, London, 1962), p. 341.

[8] R. Zallen, Gordon McKay Laboratory of Applied Science, Harvard University, Technical Report HP-12, 1964 (unpublished); R. Zallen and W. Paul, unpublished data.

coefficients in Table I and briefly discuss two examples below.

TABLE I. Pressure coefficients of some energy separations in group 4 and group 3–5 semiconductors.

Transition (low energy→high energy) group 4 element	group 3–5 compound	$\partial E/\partial P$ in units of 10^{-6} eV/bar	Representative materials measured
$\Gamma_{25'} \rightarrow \Gamma_{2'}$	$\Gamma_{15} \rightarrow \Gamma_1$	$+(10-15)$	Ge,[a] GaAs,[b] InSb[c]
$\Gamma_{25'} \rightarrow L_1$	$\Gamma_{15} \rightarrow L_1$	$+5$	Ge,[d] Sn[e]
$\Gamma_{25}' \rightarrow \Delta_1$	$\Gamma_{15} \rightarrow \Delta_1$	$-(1-2)$	Si,[f] Ge[g]
$L_{3'} \rightarrow L_1$	$L_3 \rightarrow L_1$	$+(7-8)$	Ge, GaSb, InAs[h]

[a] See Ref. 10.
[b] See Ref. 11.
[c] See Ref. 12.
[d] See Ref. 3.
[e] S. H. Groves, Gordon McKay Laboratory of Applied Science, Harvard University, Technical Report HP-10, 1963 (unpublished.)
[f] See Refs. 2 and 26.
[g] See Refs. 3 and 38.
[h] See Ref. 7.

(1) The $k=0$ vertical transition in germanium, responsible for the "direct" edge in optical absorption at 0.8 eV, takes place between a $\Gamma_{25'}$ valence band maximum and a $\Gamma_{2'}$ conduction band minimum. The transition in the zincblende structure 3–5 compounds which corresponds to $\Gamma_{25'}{}^v \rightarrow \Gamma_{2'}{}^c$ in the diamond structure group 4 elements is $\Gamma_{15}{}^v \rightarrow \Gamma_1{}^c$.[9] The pressure shift of the energy of this $\Gamma_{25'}{}^v \rightarrow \Gamma_{2'}{}^c(\Gamma_{15}{}^v \rightarrow \Gamma_1{}^c)$ transition is within the range $(10–15)\times10^{-6}$ eV/bar for Ge,[10] GaAs,[11] InSb,[12] and GaSb.[13]

(2) Germanium and many of the 3–5's exhibit doublet peaks in reflectivity in the 2–3 eV range.[14,15] These are due to $\Lambda_3{}^v \rightarrow \Lambda_1{}^c$ vertical transitions along [111] axes in the Brillouin zone.[16] The pressure coefficient of these reflectivity peaks in Ge, GaSb, and InAs is $(7–8)\times10^{-6}$ eV/bar.[7]

The results for GaP obtained in this study are consistent with this idea of correlation between pressure coefficient and transition assignment.

Comparatively little is known of the band structure of GaP. The valence band maximum is assumed to be a Γ_{15} state at the zone center, in analogy with the other 3–5 compounds.[17–19] The energy gap observed in optical absorption is 2.2 eV at room temperature, 2.33 eV at 0°K.[20–22] Measurements on GaAs–GaP alloys reveal a nonlinear variation of energy gap with composition,[23] indicating that the conduction band minimum in GaP is not the same as in GaAs, i.e., is not a Γ_1 state. This conclusion is supported by the large electron effective mass obtained from mobility and Faraday rotation experiments.[24] That the fundamental absorption edge involves indirect transitions can be seen from the functional form of the dependence of absorption coefficient upon photon energy above threshold,[21] especially the distinct phonon-derived structure observed at low temperatures.[22] The effect of pressure on the band gap is to shift it, slowly, to lower energies,[25] an unusual behavior seen also in silicon.[2,26] This suggests that the conduction band minima, as in silicon, lie along [100] directions in k space. Recent work by Spitzer and Mead on the photoresponse of surface barriers on GaAs-GaP alloys places the direct energy gap at 2.65 eV.[27] Our experiments indicate a somewhat higher estimate for this energy, closer to 2.8 eV, as will be seen in Secs. 3 and 5. Information available from ultraviolet reflectivity measurements and from measurements on an infrared absorption band in n-type material are discussed in later sections, along with our pressure experiments on these properties.

The discussion of our experimental results in Secs. 3–6 is presented in four parts. In Sec. 3 we describe the effect of pressure on the absorption edge between 2.2 and 2.7 eV, showing how the shape of the edge and its pressure dependence implies the presence of indirect transitions of the type $\Gamma_{15}{}^v \rightarrow X_1{}^c$ near 2.2 eV, and direct transitions of the type $\Gamma_{15}{}^v \rightarrow \Gamma_1{}^c$ near 2.8 eV. In Sec. 4 we discuss the 0.3-eV absorption band observed in n-type GaP, its pressure shift, and its interpretation as a direct inter-conduction band transition of the type $X_1{}^c \rightarrow X_3{}^c$. In Sec. 5 we describe the pressure shift of the strong reflectivity peak at 3.7 eV, as well as that of a weak peak at 2.8 eV not hitherto reported. We present evidence for attributing the former to $\Gamma_{15}{}^v \rightarrow \Gamma_{15}{}^c$ and the latter to $\Gamma_{15}{}^v \rightarrow \Gamma_1{}^c$ direct interband transitions. In Sec. 6 we discuss the results obtained for the effect

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[24] T. S. Moss, A. K. Walton, and B. Ellis, *Proceedings of the International Conference on Physics of Semiconductors, Exeter* (Institute of Physics and the Physical Society, London, 1962), p. 295.

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[27] W. G. Spitzer and C. A. Mead, Phys. Rev. **133**, A872 (1964).

TABLE II. Optical components used for the various experiments.

Measurement	Spectral region (eV)	Dispersing element	Spectral slit-width (eV)	Source	Detector	Fluid surrounding sample
Fundamental absorption edge	2.2–2.8	glass prism	0.004	*W* lamp	9526B photomultiplier or 1P21 photomultiplier	isopentane
Infrared absorption band	0.3–0.7	LiF prism	0.003	globar	thermocouple	CS_2
Reflectivity under pressure	2.3–4.5	NaCl prism	0.01	D_2 lamp	9526B photomultiplier	isopentane
Reflectivity at 80°K	1.9–3.2	glass prism	0.004	*W* lamp	9526B photomultiplier	vacuum
Radiative recombination at 300°K and 80°K	1.7–2.3	glass prism or 7500-Å grating	0.02 0.006	GaP diode	9526B or 7102 photomultiplier	isopentane or He gas

of pressure upon recombination radiation emitted from forward-biased *p-n* junctions of GaP. The sharp edge emission lines at 2.1–2.3 eV, observed at 80°K, serve as accurate markers for monitoring the shift of the indirect edge. The results obtained in this fashion are compared to the results of Sec. 3.

2. EXPERIMENTAL TECHNIQUES

The spectrometer used in this work was a Perkin-Elmer model 12G unit used as a prism instrument or as a grating instrument in different experiments. Usually, the prism used was glass for the visible region of the spectrum, LiF for the infrared, and NaCl for the ultraviolet. Table II lists the prisms, sources, and detectors used for the various measurements, along with the spectral resolution available in each instance. In some of the low-temperature radiative recombination work, a grating blazed at 7500 Å provided somewhat higher resolution for studying the relatively narrow (0.02-eV half-width) edge emission lines and their small pressure shift. The radiation was chopped mechanically at 13 cps and phase-detected. The resultant ac signal was then amplified, rectified, and recorded on a Leeds & Northrup type G recorder. Data were taken by continuous recording of the signal while scanning photon energy over the region of interest, rather than by a point-by-point method. Optical transmissions down to 10^{-4} were measurable before reaching the limit set by scattered light within the monochromator.

The technique of optical experiments performed at high hydrostatic pressure has been well documented elsewhere.[2,28,29] The pressure fluid was transmitted between the Bridgman press and the sample chamber by means of flexible, stainless-steel tubing.[30] Pressure was measured by means of manganin gauges,[31] calibrated by observing the freezing pressure of mercury at 0°C, 7566 bars.[32] Our experiments were conducted at pressures up to 9 kbars.[33]

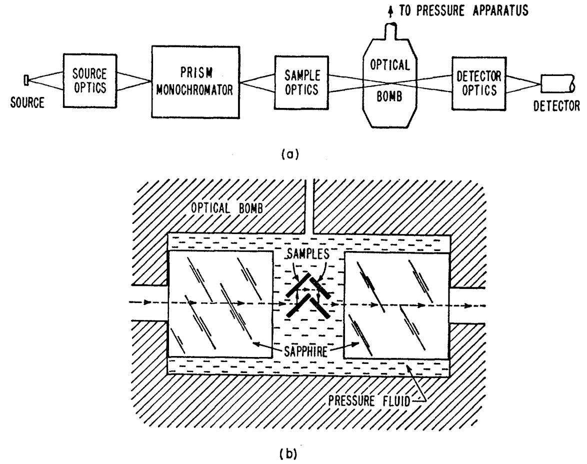

FIG. 1. Experimental arrangement for the measurement of optical absorption or reflectivity as a function of pressure: (a) block diagram of the optical system; (b) schematic diagram of the sample chamber with reflectivity samples in place. For the absorption measurements, the sample was the usual plane-parallel slab.

For the absorption and reflectivity pressure experiments, all performed at room temperature, the pressure fluids used were liquids; isopentane for the visible and ultraviolet measurements, carbon disulfide for the infrared measurements. The sample was placed in an optical high pressure vessel[34] between two $\frac{1}{2}$-in.-thick sapphire windows. A system of plane and spherical mirrors formed a real image of the monochromator exit slit at the sample position. The experimental layout is schematically shown in Fig. 1. For the measurements of absorption coefficient, the sample was a plane-parallel slab with polished surfaces normal to the direction of the light beam. For the measurements of reflectivity, four etched samples were arranged in a periscope-like reflectivity capsule. The transmission of

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[28] D. M. Warschauer and W. Paul, Rev. Sci. Instr. **29**, 675 (1958).

[29] For a bibliography of 22 references on optical high-pressure techniques, see Ref. 5, p. 442.

[30] W. Paul and D. M. Warschauer, Rev. Sci. Instr. **27**, 418 (1956).

[31] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1949).

[32] D. K. Newhall, L. H. Abbot, and R. A. Dunn, in *High-Pressure Measurement*, edited by A. A. Giardini and E. C. Lloyd (Butterworth Inc., Washington, 1963).

[33] Throughout this paper, we shall use the bar as our unit of pressure: 1 bar $\equiv 10^6$ dyn/cm^2 = 1.020 kg/cm^2 = 0.987 atm.

[34] D. Langer and D. M. Warschauer, Rev. Sci. Instr. **32**, 32 (1961).

this capsule, proportional to R^4, exhibits peaks at photon energies at which the reflectivity peaks occur. Since we were interested in the position in energy of reflectivity peaks, rather than the absolute magnitude of reflectivity, the use of 45° angle of incidence rather than normal incidence does not present any difficulties. This is supported by measurements made with this technique on Ge, InAs, and GaSb,[7] as well as on Si,[8] which yielded values of peak positions in good agreement with values obtained at normal incidence.[35,36] One feature omitted, for reasons of clarity, from Fig. 1, is a set of mirrors which sampled a small fraction of the beam from the monochromator for the purpose of monitoring the stability of the spectral distribution of the energy available in the source-monochromator-detector system.

For the low-temperature measurement of the 2.8-eV reflectivity peak discussed in Sec. 5C, the reflectivity capsule was mounted in the vacuum chamber of a conventional metal cryostat, in thermal contact with a copper block connected to the liquid nitrogen bath.

For the experiments on the emission from GaP diodes, some of which were performed at 80°K, the pressure fluid used was helium gas. This entailed the use of a second pressure system and sample chamber designed for use with gas. The diode was mounted on a combination electrical and optical plug in which a central sapphire window was encircled by electrical lead-in wires. For the low-temperature measurements, the pressure vessel was immersed in liquid nitrogen inside a stainless-steel Dewar. The radiation, emitted through the sapphire window, was conveyed by means of glass fiber optics to the source position of the spectrometer. This arrangement is schematically shown in Fig. 2.

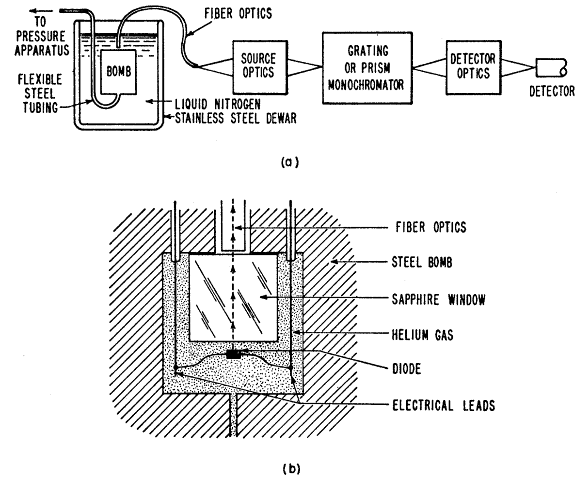

FIG. 2. Experimental arrangement for the measurement of radiative recombination as a function of pressure: (a) block diagram of the optical system; (b) schematic diagram of the sample chamber.

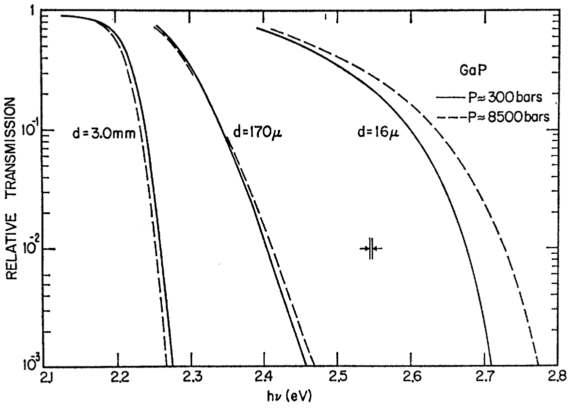

FIG. 3. Effect of pressure, at room temperature, on the optical transmission of three GaP samples. The curves have been normalized to unity in the transparent region. The two arrows show the spectral resolution used for these measurements.

3. EFFECT OF PRESSURE ON THE ABSORPTION EDGE: 2.2–2.7 eV

Transmission samples were prepared by polishing down bulk material. The range of absorption coefficient α covered in our measurements was from 5 to 5000 cm^{-1}. Figure 3 displays representative data taken at room temperature on three samples of different thickness. Relative transmission, t/t_0, where t_0 is the transmission in the transparent region at low energy, is plotted against photon energy for each sample at a low and a high pressure. Pressure shifts the transmission curves in opposite directions for the two extreme samples: There is a small shift toward lower energy for the thick sample, which spans the region of low α for $h\nu$ near 2.2 eV; and a large shift toward higher energy for the thin sample, which spans the region of high α from 2.5 to 2.7 eV. The pressure effect reverses sign within the range covered by the intermediate sample, near 2.33 eV.

Figures 4 and 5 show sets of transmission curves taken during two pressure runs. Figure 4 corresponds to absorption coefficients of the order of 10 cm^{-1}, at photon energies just above the energy gap E_G near the beginning of the absorption edge. Later we will show that the pressure shift of the curves in this region approaches the value of $\partial E_G/\partial P$, the pressure coefficient of the band gap. Figure 5 corresponds to absorption coefficients of the order of 10^3 cm^{-1}, at photon energies well into the fundamental absorption region. The change of shape with pressure is readily apparent; the large positive shift increases rapidly with $h\nu$. The large difference between the ranges of photon energy covered in Figs. 4 and 5 illustrates the difference in magnitude between the small, negative shift with pressure near 2.2 eV, and the large, positive shift with pressure near 2.7 eV.

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[35] J. Tauc and A. Abraham, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechslovakian Academy of Sciences, Prague, 1961), p. 375.

[36] M. Cardona, J. Appl. Phys. **32**, 2151 (1961).

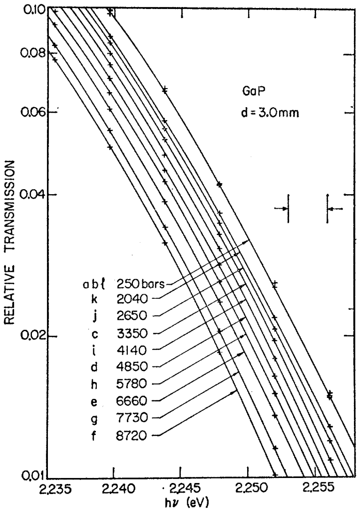

FIG. 4. A pressure run taken on a thick sample. The letters, arranged alphabetically, give the order in which the data were taken.

Plots such as Figs. 4 and 5 were used to construct isoabsorption curves, $h\nu_\alpha = h\nu_\alpha(P)$, in which photon energy for a given relative transmission (i.e., for a given α) is plotted against pressure. These were linear, within our 0–9 kbar pressure range. In Fig. 6 the slopes of these lines, $(\partial h\nu/\partial P)_\alpha$, are shown as a function of their zero-pressure intercepts $h\nu(0)$. The two extreme points, at 2.78 and 2.23 eV, are obtained from other experiments to be discussed in Secs. 5 and 6, respectively. All that need be noted now is that they are consistent with the isoabsorption data spanning the range from 2.24 to 2.72 eV. Figure 6 essentially summarizes the effect of hydrostatic pressure on the room temperature absorption edge of GaP.

To obtain $\partial E_G/\partial P$ from Fig. 6, it is necessary to know the room temperature value of E_G. One method of studying an indirect edge is a high-resolution analysis of phonon-absorption and phonon-emission components of $\alpha(h\nu)$ at low α, as has been successfully performed for Ge and Si.[37] Gershenzon, Thomas, and Dietz[22] have made such a study on GaP at low temperatures, observing phonon-emission components consistent with previous work on phonon combination bands in GaP. Their work is the most direct evidence thus far reported that the energy gap is indirect, and provides the best estimate available for E_G. Although unable to observe phonon structure at room temperature, they extrapolate their low-temperature data to a room-temperature energy gap of 2.22 eV.

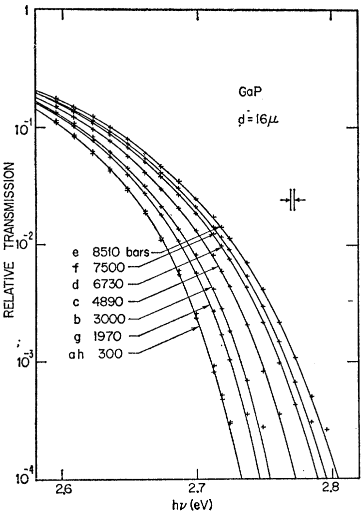

FIG. 5. A pressure run taken on a thin sample. The letters, arranged alphabetically, give the order in which the data were taken.

Using $E_G = 2.22$ eV, we find from Fig. 6 that

$$\partial E_G/\partial P = -1.2 \times 10^{-6}\ \text{eV/bar}. \tag{1}$$

This pressure coefficient is in fairly good agreement with previously reported values, less accurately determined than the present one, although it is somewhat smaller in magnitude.[25] The band gap of silicon, a $\Gamma_{25'}{}^v \to \Delta_1{}^c$ indirect transition from the valence band maximum at the zone center to conduction band minima near the zone boundary along [100] axes, has a pressure coefficient of -1.5×10^{-6} eV/bar.[2,26] In germanium, the corresponding $\Gamma_{25'}{}^v \to \Delta_1{}^c$ energy separation also has a small, negative pressure coefficient lying between 0 and -2×10^{-6} eV/bar[3]; the most accurate value is -1.5×10^{-6} eV/bar.[38] Thus the GaP band gap coefficient is similar to the coefficient of $\Gamma_{25'}{}^v \to \Delta_1{}^c$ in silicon and germanium. In all three cases the energy separation slowly decreases with pressure. This may be contrasted to the behavior of the band gap of germanium, a $\Gamma_{25'}{}^v \to L_1{}^c$ indirect transition, which increases with pressure at a rate of $+5\times10^{-6}$ eV/bar.[3]

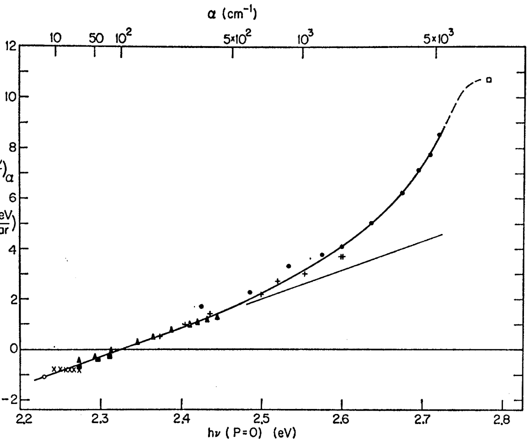

FIG. 6. The pressure dependence of the GaP absorption edge. Sample thickness (μ): 16 ●; 29 +; 170 ▲; 550 ■; 3000 ×. Also, reflectivity peak □, edge emission ○.

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[37] T. P. McLean, Progr. Semiconductors **5**, 53 (1960).

[38] W. E. Howard, Gordon McKay Laboratory of Applied Science, Harvard University, Technical Report HP-7, 1961 (unpublished).

We conclude then that the indirect transition responsible for the energy gap in GaP is that which corresponds to the $\Gamma_{25'}{}^{v} \rightarrow \Delta_1{}^{c}$ transition in Ge and Si, namely, $\Gamma_{15}{}^{v} \rightarrow \Delta_1{}^{c}$. Since the degeneracy at the X point in the diamond structure is split in the zincblende structure, it is likely that the conduction-band minima in GaP are at the X point on the zone boundary, rather than along the Δ axis in the interior of the zone. Thus we assign the band gap to the transition $\Gamma_{15}{}^{v} \rightarrow X_1{}^{c}$.

Figure 6 clearly shows that the absorption edge does not simply translate rigidly in energy along with E_G when pressure is applied, since for that situation $(\partial h\nu/\partial P)_\alpha$ would be equal to $\partial E_G/\partial P$ for all $h\nu$. Instead, $(\partial h\nu/\partial P)_\alpha$ varies linearly with $h\nu$ between 2.2 and 2.45 eV, beyond which energy it increases progressively more rapidly. Thus, for example, the photon energy corresponding to $\alpha = 5000$ cm^{-1} increases with pressure at a rate of 8×10^{-6} eV/bar, even though E_G itself decreases with pressure.

To account for the variation of $(\partial h\nu/\partial P)_\alpha$ with $h\nu$, we must first discuss the theoretically calculated and the experimentally measured shape of the absorption edge, $\alpha = \alpha(h\nu)$. The simplest theory[37] predicts that for indirect, allowed transitions, α is given by a sum of terms corresponding to phonon emission and absorption processes, and that each term varies quadratically with energy above threshold. Thus,

$$\alpha = \sum_i (\alpha_i{}^{+} + \alpha_i{}^{-}), \tag{2}$$

where:

$$\alpha_i{}^{\pm} = \begin{cases} 0, & \Delta E_i{}^{\pm} < 0 \\ C_i{}^{\pm}(\Delta E_i{}^{\pm})^2, & \Delta E_i{}^{\pm} > 0 \end{cases} \quad \begin{aligned} &\Delta E_i{}^{\pm} = h\nu - E_G{}^{i\pm}, \\ &E_G{}^{i\pm} = E_G \pm k\theta_i. \end{aligned}$$

Here $\alpha_i{}^{+}$ is the component due to emission of a phonon of energy $k\theta_i$, $\alpha_i{}^{-}$ is the component due to absorption of a phonon of energy $k\theta_i$. In the more exact theory,[37,39] which includes the effect of the electron-hole interaction (excitons), it is shown that each phonon component, $\alpha_i{}^{\pm}$, is itself composed of several contributions starting at a series of energies given by $E_G{}^{i\pm} - (1/n^2)E_{\text{ex}}$, where E_{ex} is the exciton binding energy and n is a positive integer. For allowed transitions, each contribution for finite n (formation of bound electron-hole pairs) goes as $(\Delta E)^{1/2}$ for small ΔE, the energy above threshold. The highest threshold contribution, starting at $h\nu = E_G{}^{i\pm}$ (formation of unbound electron-hole pairs), goes as $(\Delta E)^{3/2}$ for small ΔE.

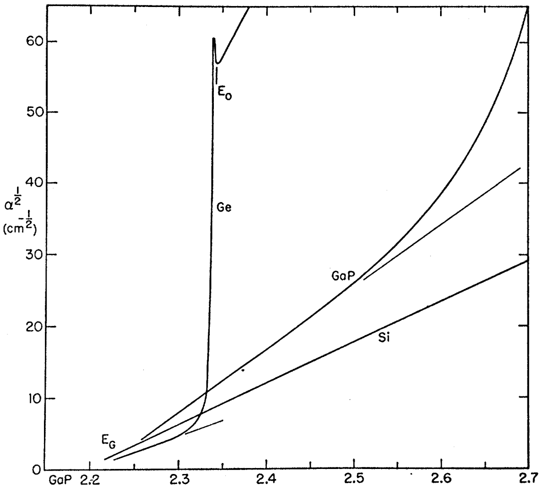

FIG. 7. A comparison of the absorption edges of Ge, Si, and GaP. The curves have been shifted horizontally so that the indirect energy gaps coincide. The Ge data (which are for 20°K) and the Si data (which are for 77°K) are from T. P. McLean, Progr. Semiconductors **5**, 53 (1960). The GaP curve is our room-temperature, zero-pressure data.

When experimental data on an indirect edge is analyzed, it is usual to construct a plot of $\alpha^{1/2}$ versus $h\nu$. From the above it is clear that $\alpha^{1/2}$ versus $h\nu$ would not be expected to reveal simple linear behavior in the complex region near $h\nu \approx E_G$. However, in the region in which $h\nu$ greatly exceeds the highest phonon-emission threshold ($h\nu - E_G{}^{i} \gg E_{\text{ex}}$ for all i), the simple theory and the theory including excitons both give the same result:

$$\alpha = C[(h\nu - E_G{}')^2/h\nu]. \tag{3}$$

The quantity $E_G{}'$ results from a weighted average of the phonon components and may differ from E_G by an amount of the order of a phonon energy. This expression holds provided that the assumption of parabolic energy bands, used in the theories, is valid to these energies. The factor $(h\nu)^{1/2}$ usually does not vary by more than 10% over the range of interest, so that we might expect $\alpha^{1/2}$ versus $h\nu$ to exhibit a region of linearity at photon energies exceeding $E_G + 0.05$ eV.

Our results on the room temperature, atmospheric pressure absorption edge of GaP are in quite good agreement with the data of Spitzer, Gershenzon, Frosch, and Gibbs[21] (henceforth referred to as SGFG). Figure 7 presents a comparison of the absorption edge of GaP with those of Ge and Si. The scales of photon energy have been shifted so that the indirect energy gaps roughly coincide. The vertical scale is the square root of the absorption coefficient $\alpha^{1/2}$. The germanium and silicon data, for 20° and 77°K, respectively, are from the work of Macfarlane *et al.* quoted in Ref. 37. The silicon edge is accurately linear over the range shown, extrapolating to $\alpha^{1/2} = 0$ at a photon energy of 1.19 eV, 0.03 eV higher than the actual band gap at 77°K. The germanium edge is linear over a small range of energy until the onset of direct transitions at E_0, the direct energy gap. The extrapolated energy is 0.74 eV, in agreement with E_G (to the nearest 0.01 eV). The GaP edge is linear below about 2.5 eV, extrapolating to zero absorption at 2.20 eV, 0.02 eV lower than the band gap as estimated by Gershenzon *et al.* Above

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[39] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

2.5 eV, the absorption coefficient increases progressively more rapidly than the $(h\nu-2.2\text{ eV})^2$ dependence obeyed between 2.25 and 2.5 eV.

The GaP absorption edge and its pressure dependence may be represented, in the 2.2–2.5-eV energy range (the region of linear behavior in Figs. 6 and 7) by the expression

$$\alpha^{1/2}(h\nu,P)=A(P)[h\nu-E_G(P)]. \qquad (4)$$

This is equivalent to (3) with the approximations $E_G'=E_G$ and $(h\nu)^{-1/2}=\text{constant}$. If we regard $h\nu=h\nu(\alpha,P)$ as the dependent variable, then partial differentiation of (4) yields, to lowest order in P,

$$\left(\frac{\partial h\nu}{\partial P}\right)_\alpha=\frac{\partial E_G}{\partial P}-\frac{1}{A}\frac{\partial A}{\partial P}[h\nu-E_G(0)]. \qquad (5)$$

This is just the observed linear variation of $(\partial h\nu/\partial P)_\alpha$ with $h\nu$ shown in Fig. 6, where $(\partial h\nu/\partial P)_\alpha=\partial E_G/\partial P$ at $h\nu=E_G(0)$, and where the slope of the linear region, $(d/dh\nu)(\partial h\nu/\partial P)_\alpha\equiv\beta$, is given by $-(1/A)(\partial A/\partial P)$. In Sec. 7, the quantity β is estimated theoretically from the proposed pressure-dependent band structure of GaP. The result is in satisfactory agreement with the measured value of $1.15\times10^{-5}\text{ bar}^{-1}$ obtained from Fig. 6.

In the region of photon energy above 2.5 eV, the curves of Figs. 6 and 7 deviate from their linear behavior at lower energy. Both $\alpha^{1/2}$ and $(\partial h\nu/\partial P)_\alpha$ increase, gradually at first and then more and more rapidly, above the line extrapolated from low energies. The suggestion which immediately comes to mind is that a new mechanism, strongly pressure-dependent, is beginning to contribute to the absorption above 2.5 eV.

Several possible explanations for the rise in absorption are listed below:

(a) the breakdown of the validity of the theory behind (3), due to such considerations as the k dependence of matrix elements, energy denominators, and especially, effective masses (nonparabolic energy bands away from the extrema);

(b) the onset of a new indirect transition process at 2.5 eV, involving, for example, a set of higher conduction band minima;

(c) the low-energy "tail" of a direct edge occurring at a higher energy not reached in our absorption measurements;

(d) the onset of direct transitions at 2.5 eV.

Both (a) and (b) are plausible possibilities. The valence and conduction band masses may increase at k vectors away from the extrema, thereby providing a joint density of states for indirect transitions exceeding that predicted on the basis of parabolic bands. Also, regarding (b), it will be seen in Sec. 4 that there is evidence for a higher conduction band lying, at the X point, about 0.3 eV above the lowest conduction band. However, our calculations indicate that these two mechanisms are probably too weak to account for the observed increase in α above 2.5 eV. Note, for example, that (a) is apparently unimportant in the case of silicon, for which $\alpha^{1/2}$ versus $h\nu$ is linear over the 0.5-eV range of photon energy shown in Fig. 7. If the additional contribution to the absorption of GaP is analyzed by constructing $\alpha_2\equiv\alpha-\alpha_1$, where α_1 is extrapolated from the low-energy region where $\alpha=\alpha_1=A(h\nu-2.2\text{ eV})^2$, then it is found that α_2 does not at all resemble the $(h\nu-2.5\text{ eV})^2$ dependence expected of an indirect transition beginning at 2.5 eV, but increases much more rapidly than this. Thus, neither (a) nor (b) accounts for the observed shape of the edge. Moreover, neither mechanism readily accounts for the more rapid increase of $(\partial h\nu/\partial P)_\alpha$ with $h\nu$ above 2.5 eV.

If the minimum "vertical" separation between the valence and conduction bands in GaP occurs at $k=0$ and the transition involved is of the type $\Gamma_{15}{}^v\rightarrow\Gamma_1{}^c$, as is the case in several other 3–5 compounds, then the pressure coefficient of the direct gap, $\partial E_0/\partial P$, is expected to have a value in the range of $+10$ to $+15\times10^{-6}$ eV/bar. Mechanisms (c) and (d) would then predict an increase of $(\partial h\nu/\partial P)_\alpha$ toward the value of $\partial E_0/\partial P$. In germanium it is found that $(\partial h\nu/\partial P)_\alpha$ reaches the value of the direct gap coefficient at an energy somewhat less than E_0, and then levels off.[10] For GaP we see that $(\partial h\nu/\partial P)_\alpha$ is still below the expected value of $\partial E_0/\partial P$ at $h\nu=2.7$ eV, indicating that E_0 occurs at a higher energy. Thus, only (c) is consistent with the variation of $(\partial h\nu/\partial P)_\alpha$ of Fig. 6. SGFG proposed (d) to account for the increase in α above 2.5 eV, and to account for an infrared absorption band observed in n-type material. Our discussion in this section favors (c) as the explanation for the increase in α; the actual origin of the infrared absorption band will be discussed in Sec. 4.

In a direct absorption edge, the absorption coefficient rises rapidly to a high value at E_0, and then increases more slowly with $h\nu$.[37,40] The direct edge of Ge is shown in Fig. 7, and clearly exhibits the characteristic "knee" at E_0. This curve is for 20°K and shows the exciton peak at an energy just under E_0. At room temperature the exciton peak is washed out but the marked knee at E_0 persists. No indication of such a knee appears in the GaP absorption edge of Fig. 7. This also demonstrates that E_0 does not fall within the range shown, and that it thus exceeds 2.7 eV.

From these arguments we therefore propose that (c) is the dominant mechanism responsible for the deviation from linearity above 2.5 eV in Figs. 6 and 7. The presence of a $\Gamma_{15}{}^v\rightarrow\Gamma_1{}^c$ direct transition is indicated at an energy E_0 greater than 2.7 eV. The momentum matrix element for this transition, p_{cv}, which governs the optical absorption, is nearly equal for several 3–5 compounds.[41] Assuming that the same value holds also

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[40] M. D. Sturge, Phys. Rev. **127**, 768 (1962).

[41] H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).

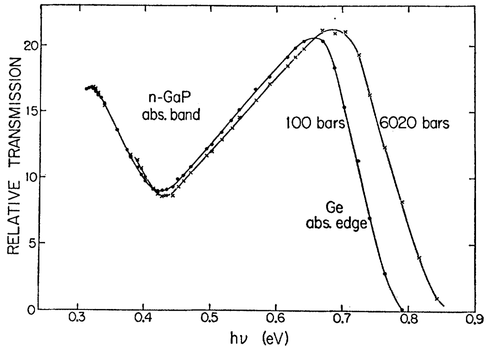

FIG. 8. Effect of pressure on the infrared absorption band in n-type GaP. The trough at 0.4 eV is due to the GaP absorption band. The cutoff at 0.7–0.8 eV is due to the absorption edge of a Ge sample which was included along with the GaP sample in order to provide a comparison of pressure shifts.

for GaP, we can obtain a rough estimate for $\alpha(E_0)$, the absorption level at the knee of the absorption curve. This quantity is proportional to $p_{cv}^2 m_c^2/n^3 E_0$,[37,39] where n is the refractive index, and where it is assumed thta both the density-of-states effective mass and the exciton reduced mass are determined primarily by m_c, the conduction band effective mass. In first approximation, m_c is proportional to E_0,[41] so that $\alpha(E_0)$ becomes proportional to $p_{cv}^2 E_0/n^3$. For GaAs, $\alpha(E_0)$ is equal to 0.9×10^4 cm^{-1}.[40] Using the values of n and E_0 for GaAs and GaP, where a trial value of $E_0=3$ eV is assumed for GaP, we obtain $\alpha(E_0)\approx2\times10^4$ cm^{-1} for GaP. The absorption curve of Fig. 7 extrapolates to this level at a photon energy of about 2.75–2.80 eV. In Sec. 5C we shall discuss a weak peak appearing in the reflectivity spectrum of GaP at about 2.78 eV, which we attribute to the $\Gamma_{15}^v \rightarrow \Gamma_1^c$ direct edge.

4. EFFECT OF PRESSURE ON AN INFRARED ABSORPTION BAND IN n-TYPE GaP

SGFG reported an absorption band in n-type GaP, in excess of the normal free carrier absorption, with a strength proportional to the electron concentration.[21] At room temperature, the band peaks at 0.41 eV and its low-energy threshold is at 0.31 eV; at low temperatures the threshold shifts to higher energy by about 0.05 eV. Since the absorption is proportional to the concentration of electrons, the initial states of the transitions responsible are probably either at the conduction band minima, or at shallow impurity states derived from these minima.

Spitzer *et al.* suggested that the mechanism responsible is an indirect transition from the conduction band minima to a higher minimum at $k=0$, i.e., $X_1^c \rightarrow \Gamma_1^c$. As a test of this hypothesis, which is inconsistent with our previously discussed estimate of the energy of Γ_1^c, we measured the effect of pressure on the absorption band in samples kindly provided us by Dr. Spitzer. Since $\partial E_0/\partial P$ exceeds $+10\times10^{-6}$ eV/bar, and $\partial E_G/\partial P$ is negative, the pressure shift of E_0-E_G (the energy of the $X_1^c \rightarrow \Gamma_1^c$ transition) should definitely exceed $+10\times10^{-6}$ eV/bar. Figure 8 displays the optical transmission, at a low and a high pressure, of an n-type GaP sample ($n=10^{18}$ cm^{-3}, $d=0.1$ mm) in series with a Ge sample included for purposes of comparison. The shift of the high-energy cutoff near 0.75 eV, due to the Ge, is $+9\times10^{-6}$ eV/bar. The shift of the dip in transmission caused by the absorption band is seen to be very much smaller than this, almost an order of magnitude smaller than that expected. This is strong evidence against this particular mechanism.

In an earlier paper, one of us (W.P.) presented an explanation of this band based on vertical transitions of conduction electrons to the next higher conduction band.[4] This simple model, unlike the indirect scattering process discussed above, leads naturally to a definite low-energy threshold, especially if the electrons are initially weakly bound to shallow impurities. It also explains reasonably well the magnitude of the absorption band and its relative insensitivity to temperature, as no phonons are involved. The model is consistent with a small pressure coefficient. Recently, Allen and Hodby[42] have studied this absorption band in n-type GaAs-GaP alloys. They found that it appears only in the alloys which have the (100) minima lowest, strong evidence in favor of our model.

The higher conduction band providing the final states for these direct transitions is logically X_3^c, which is degenerate with X_1^c in diamond-structure materials like Ge and Si. Thus the $X_1^c \rightarrow X_3^c$ energy separation in GaP is about 0.3 eV. Values for this quantity for some of the other 3–5's have been estimated by Greenaway[43] from structure observed at low temperatures in the strong X-point reflectivity peak in the ultraviolet. He obtains values in the range of 0.4–0.5 eV, close to the GaP value. The interconduction band absorption in n-type GaP which has been discussed here is the analog of the intervalence band infrared absorption found in p-type Ge,[44] GaAs,[45] and InAs;[46] the shape of the absorption curve is similar in all of these materials.

5. THE EFFECT OF PRESSURE ON THE REFLECTIVITY SPECTRUM: 2.5–4.5 eV

A. Reflectivity Spectra

Reflectivity spectra of semiconductors exhibit peaks in the 1–10-eV range of photon energies, due to corners (peaks or edges) in dN/dE, the joint density-of-states for direct interband transitions.[14–16] Corners in dN/dE are correlated with critical points in k space of $E^{cv}(k)$

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[42] J. W. Allen and J. W. Hodby, Proc. Phys. Soc. **82**, 315 (1963).

[43] D. L. Greenaway, Phys. Rev. Letters **9**, 97 (1962).

[44] H. B. Briggs and R. C. Fletcher, Phys. Rev. **87**, 1130 (1952); *ibid.* **91**, 1342 (1953).

[45] R. Braunstein, Phys. Chem. Solids **8**, 280 (1959).

[46] F. Stern and R. M. Talley, Phys. Rev. **108**, 158 (1957).

$=E^c(k)-E^v(k)$, the vertical separation of the conduction and valence bands. The critical points are of four types; minima, maxima, and two types of saddle points. The saddle points produce the strongest singularities in dN/dE, and it is their identifications with particular reflectivity peaks which are the most certain. The strongest reflectivity peak in Ge, Si, and the 3–5 compounds appears at about 4 or 5 eV and is due to saddle point singularities at X and Σ points[47] in the zone.[14,16] Doublet peaks appearing in the 2–3 eV range in Ge and some of the 3–5's are due to saddle points at Λ points[47] in the zone,[16] the doublet structure being due to the spin-orbit splitting of the valence band.

Reflectivity peaks have been reported for GaP at 3.7, 5.3, 6.9, and 10 eV.[15] The dominant 5.3-eV peak is supposed due to the X, Σ critical point transition.[14,16] The $L_3{}^v \to L_3{}^c$ (or $\Lambda_3{}^v \to \Lambda_3{}^c$) transition has been suggested for the 6.9-eV peak. No transition has been associated with the peak at 10 eV. The 3.7-eV peak may be due to $\Lambda_3{}^v \to \Lambda_1{}^c$ transitions, in analogy with the 2–3-eV peaks in Ge and some of the 3–5's; or it may be due to $\Gamma_{15}{}^v \to \Gamma_{15}{}^c$ transitions, in analogy with the $\Gamma_{25'} \to \Gamma_{15}{}^c$ transitions believed responsible for the first peak in Si at 3.4 eV.[14,36]

In this section we shall discuss measurements which we have made on the reflectivity between 2.5 and 4.5 eV. We have measured the effect of pressure on the peak at 3.7 eV, as well as on a weak peak at 2.8 eV which has not been reported previously.

B. The Reflectivity Peak at 3.7 eV

Figure 9 shows the effect of pressure on the 3.7-eV peak. The vertical scale is the transmission of a reflectivity capsule (four successive 45° reflections from etched surfaces) of GaP immersed in isopentane, and is proportional to R^4. The peak position shifts toward higher energies at the rate of $+(5.8\pm 15\%)\times 10^{-6}$ eV/bar. In Table III we have compared the pressure and temperature coefficients of this peak with those of the first peak in silicon and the Λ-point doublet peaks in germanium and other materials. Although there is usually little relationship between temperature coefficients belonging to a given type of transition, the temperature coefficients of the Λ-point peaks are all about the same.[48] The pressure coefficients of Table III were measured in this laboratory; the temperature coefficients are taken from the literature.[36,48] The GaP and Si coefficients are alike, and seem to be significantly smaller than the Λ-point coefficients. These data indicate that the same mechanism is probably responsible for the GaP and Si peaks, and that it is not a Λ-point transition.[49]

TABLE III. Comparison of the behavior of the 3.7-eV reflectivity peak in GaP with that of some other reflectivity peaks.

Coefficient	$\Lambda_3 \to \Lambda_1$ peaks at 2–3 eV in Ge, GaAs, GaSb, etc.	Peak at 3.7 eV in GaP	Peak at 3.4 eV in Si
$(\partial E/\partial P)_T$ in 10^{-6} eV/bar ($\pm 10\%$)	$+7.2^a$	$+5.8$	$+5.2^b$
$(\partial E/\partial T)_P$ in 10^{-4} eV/°K ($\pm 20\%$)	$-4.7^{c,d}$	-2.5^c	$-2.6^{c,d}$

[a] See Ref. 7. [b] See Ref. 8. [c] See Ref. 36. [d] See Ref. 48.

That the Si 3.4-eV peak is other than a Λ-point transition has already been conclusively established by work of Tauc and Abraham[50] on Ge-Si alloys, in which it was shown that the variation of the energy of the first reflectivity peak (followed as a function of composition) shows a definite break at about 79% silicon. It now remains to identify this peak, and thereby the GaP 3.7-eV peak. There is a burgeoning body of evidence that the $\Gamma_{25'}{}^v \to \Gamma_{15}{}^c$ energy separation in silicon is

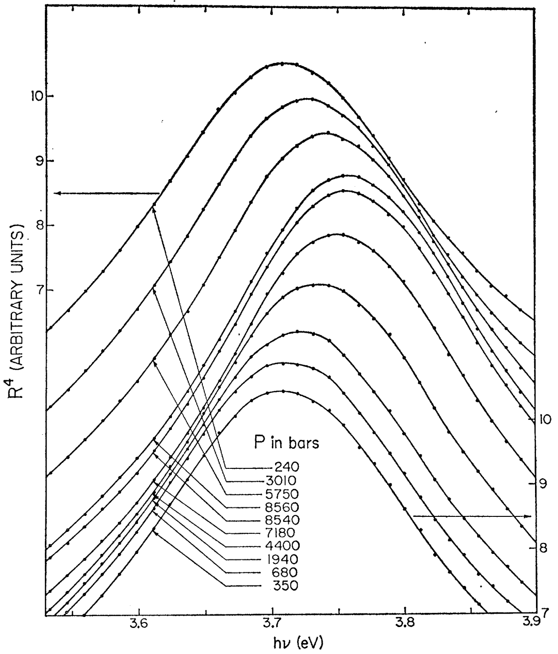

FIG. 9. Effect of pressure on the GaP reflectivity peak at 3.7 eV. The curves have been shifted vertically in order to separate them. The pressures are listed in the order in which the data were taken.

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[47] We are using the accepted notation for various positions of high symmetry in the Brillouin zone of a face-centered cubic lattice: Γ, (000); Δ, along [100] axes; X, (100) at the zone boundary; Σ, along [110] axes; K, (110) at the zone boundary; Λ, along [111] axes; L, (111) at the zone boundary.

[48] F. Lukes and E. Schmidt, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (Institute of Physics and the Physical Society, London, 1962), p. 389.

[49] It is worth noting that the lack of observed doublet structure in the Si and GaP peaks does not, by itself, make the Λ-point explanation unlikely, since the expected spin-orbit splitting in these materials is small, less than 0.1 eV (Ref. 18).

[50] J. Tauc and A. Abraham, Phys. Chem. Solids **20**, 190 (1961).

3.4 eV.[51–54] The band calculations for silicon seem to have successfully accounted for the reflectivity spectrum,[52] photoemission experiments on silicon surfaces,[52,53] and the alloy experiments mentioned above. We therefore assign the 3.4-eV Si peak to $\Gamma_{25'}^{v}\rightarrow\Gamma_{15}^{c}$. We conclude then that the 3.71-eV reflectivity peak in GaP is due to $\Gamma_{15}^{v}\rightarrow\Gamma_{15}^{c}$ transitions ($\Gamma_{25'}^{v}$ in Si corresponds to Γ_{15}^{v} in GaP).

GaP belongs to the isoelectronic sequence GeSi, GaP, ZnS, CuCl. All of these materials exhibit very similar reflectivity spectra,[15,50,55,56] each peak occurring at an energy which is higher the more polar the compound. The data of Tauc and Abraham[50] indicate that the energies of the $\Gamma_{25'}^{v}\rightarrow\Gamma_{15}^{c}$ and $\Lambda_3^{v}\rightarrow\Lambda_1^{c}$ transitions in GeSi are 3.1 and 2.9 eV, respectively. Cardona,[56] from work on CuBr-CuCl alloys, puts the corresponding energies in CuCl at 6.8 and 6.5 eV. In both materials only a single reflectivity peak is observed, the weaker peak apparently being hidden under the stronger (which is less than 0.3 eV away). Cardona suggests that this is likely also the case in the other two members of the series. This would place the $\Lambda_3^{v}\rightarrow\Lambda_1^{c}$ energy separation in GaP in the 3.5–4.0-eV range where, in reflectivity, it is hidden under the (in this case) stronger $\Gamma_{15}^{v}\rightarrow\Gamma_{15}^{c}$ peak at 3.7 eV. A study of reflectivity in the alloy system GaAs-GaP would determine whether or not this is the correct picture. Finally, corroborating evidence for the Γ-point assignment to the 3.7-eV peak in GaP comes from the corresponding peak in ZnS which shows no splitting under the use of polarized light, and is therefore due to transitions at $k=0$.[57]

C. The Reflectivity Peak at 2.8 eV

In Sec. 3 we estimated a value of about 2.8 eV for E_0, the $\Gamma_{15}^{v}\rightarrow\Gamma_1^{c}$ direct gap. This type of direct edge, at which there is a sharp rise (edge) in dN/dE due to a minimum in $E^{cv}(k)$, is much weaker than other direct transitions: Typical values of α for this edge are of the order of 10^4 cm^{-1},[37,40] while typical values of α in the region of (for example) the $\Lambda_3^{v}\rightarrow\Lambda_1^{c}$ and the $X_4\rightarrow X_1$ transitions are of the order of 10^6 cm^{-1}.[15,58] It is therefore not surprising that for Ge, no structure has yet been reported in the reflectivity spectrum near $E_0=0.8$ eV. For GaAs, there is some evidence of weak structure near $E_0=1.5$ eV.[46] Structure near 2.8 eV has not been present in published reflectivity spectra of GaP.

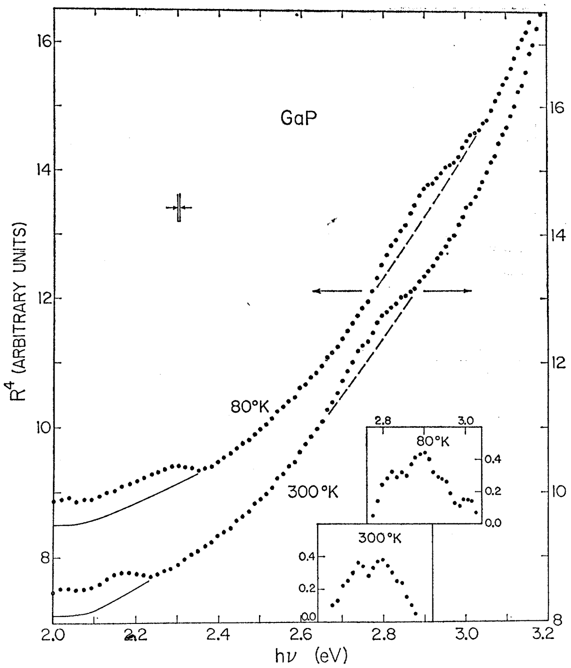

Fig. 10. Effect of temperature on the GaP reflectivity peak at 2.8 eV. The inserts show the data obtained by subtracting out the smooth background.

We have examined the transmission of a reflectivity capsule of GaP in the vicinity of 2.8 eV. Figure 10 shows the transmission (proportional to R^4) of the capsule in vacuum at 300 and 80°K. [It was found that the arrangement of the samples accidentally placed a small transmission sample (thickness about 1 mm) effectively in parallel with the R^4 samples. This is responsible for the small additional contribution to the transmission below about 2.3 eV. The shift of the cutoff of this added component yields a value of $-(5.2\pm15\%)\times10^{-4}$ eV/°K for $\partial E_G/\partial T$, the temperature coefficient of the indirect gap, in agreement with a previously reported value[20] of -5.4×10^{-4} eV/°K.] Superimposed upon the rapid rise of R^4 toward the 3.7-eV peak, there is very weak structure near 2.8 eV. This takes the form of a peak having a height of the order of $\Delta R^4/R^4\approx1/30$, and a width at half-maximum of about 0.2 eV. The temperature coefficient of the peak position is $-(4.6\pm15\%)\times10^{-4}$ eV/°K.

Figure 11 shows the effect of pressure on the 2.8-eV "peak," measured at room temperature, with the samples immersed in isopentane. Its pressure coefficient is $+(10.7\pm15\%)\times10^{-6}$ eV/bar. This large coefficient is appropriate for a $\Gamma_{15}^{v}\rightarrow\Gamma_1^{c}$ direct transition.[3–6] It has been plotted as the high-energy point in Fig. 6 (at 2.78 eV, the zero-pressure photon energy of the peak), where it is seen to be consistent with the absorption edge data obtained at lower energies.

Structure in reflectivity in this region (where the extinction coefficient, $K\equiv(C/2\omega)\alpha\approx10^{-5}$ cm$\times\alpha$, is less than unity) closely follows structure in the refractive

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[51] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).

[52] D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962).

[53] W. E. Spicer and R. E. Simon, Phys. Rev. Letters **9**, 385 (1962).

[54] F. Bassani and D. Brust, Phys. Rev. **131**, 1524 (1963).

[55] W. C. Walker and J. Ostantowski, J. Opt. Soc. Am. **53**, 399 (1963); M. Cardona, Phys. Rev. **129**, 1068 (1963).

[56] M. Cardona, Phys. Rev. **129**, 69 (1963).

[57] M. Cardona, Solid State Communications **1**, 109 (1963).

[58] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1958); **120**, 37 (1960).

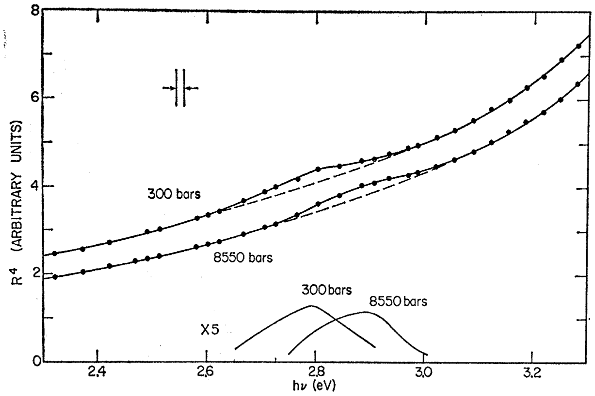

FIG. 11. Effect of pressure on the GaP reflectivity peak at 2.8 eV. The lower curves show the result of subtracting out the smooth background.

index n.[58,59] From the magnitude of $\Delta R^4/R^4$ of the 2.8-eV peak in Figs. 10 and 11, we deduce a value of about 0.02 for Δn, of the order of values calculated by Stern for n near E_0 in GaAs.[60] This value of Δn is about a factor of 10^2 smaller than the values for the first strong reflectivity peaks belonging to edges rising to $\alpha \approx 10^6$ cm^{-1},[58] implying that the edge involved has a strength of about 10^4 cm^{-1}.

From this evidence we conclude that this weak reflectivity peak is due to the onset of direct transitions of the type $\Gamma_{15}{}^v \rightarrow \Gamma_1{}^c$ at the center of the zone. The pressure and temperature dependence of the direct gap is then given by

$$E_0 = 2.78 + (10.7 \pm 15\%) \times 10^{-6} P - (4.6 \pm 15\%) \times 10^{-4} (T - 300), \quad (6)$$

where E_0 is in electron volts, P is in bars, T is in degrees Kelvin. Recently, Spitzer and Mead have estimated a value for E_0 of 2.65 eV based on measurements of the photoresponse of metal-semiconductor surface barriers on GaAs-GaP alloys.[27] We do not know the reason for the difference between our two results.

The photoconductivity of GaP shows a sharp drop at about 2.8 eV.[61] Similar effects have been observed in other materials,[62] and have been accounted for by the production of photoelectrons at $k=0$, where they contribute little to the current because of rapid direct recombination.[63] This is consistent with our estimate of E_0.

Note added in proof. D. F. Nelson, L. F. Johnson, and M. Gershenzon [Bull. Am. Phys. Soc. **9**, 236 (1964)] have recently observed structure in the photoconductivity spectra of GaP samples which they attribute to direct exciton formation. Their room-temperature estimate of E_0, 2.79 eV, is in excellent agreement with our result, as is the temperature dependence which they obtain for E_0. The agreement between these two independent determinations of the direct gap is strong evidence for the correctness of our interpretation of this reflectivity peak, as discussed above.

6. EFFECT OF PRESSURE ON RADIATIVE RECOMBINATION IN FORWARD-BIASED *p-n* JUNCTIONS

Diodes formed from GaP *p-n* junctions exhibit carrier-injection electroluminescence (EL) emission of low efficiency when biased in the forward direction.[64,65] At low temperatures the emission in the green, at or near E_G, reveals a great deal of very complicated and interesting fine structure[65–67] due to such effects as associated shallow donor-acceptor pairs[66] and bound exciton states.[67] There is also a broad emission in the red involving levels well inside the forbidden zone.[64]

We have measured the effect of pressure on some of the EL lines observed in GaP diodes. A reason for doing this is that sharp lines emitted with nearly the band-gap energy serve as accurate and convenient markers for monitoring the pressure shift of the band gap, as has been demonstrated for GaAs.[11] We can thus obtain in straightforward fashion an independent measurement of $\partial E_G/\partial P$ to compare with the result of the analysis given in Sec. 3 of the pressure dependence of $\alpha(h\nu)$.

Table IV summarizes our data on two green-emitting diodes fabricated at Bell laboratories by diffusing Zn into nonintentionally doped, epitaxially grown, n-type material. The diodes were provided to us by Dr. M.

TABLE IV. Effect of pressure on GaP radiative recombination lines emitted at near band-gap energy.

Temp. (°K)	Emission line[a,b]	$h\nu$ (eV)	$\Delta h\nu$[c] (eV)	Relative intensity[d]	$-\partial h\nu/\partial P$ (10^{-6} eV/bar)
80	EE–2LO	2.096	0.04	6	...
80	EE–LO	2.145	0.04	25	1.0±0.1
80	EE	2.194	0.04	100	1.0±0.1
80	A–Ac–LO	2.238	0.02	60	1.2±0.1
80	A–Ac	2.294	0.02	10	1.4±0.5
80	A	2.308	0.02	2	1±1
300	...	2.23	0.1	...	1.1±0.1

[a] See Ref. 65.
[b] EE is edge emission, A is an exciton line, LO is longitudinal-optical phonon, Ac is acoustical phonon.
[c] Approximate full width at half-maximum.
[d] At a current of 10 mA.

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Gershenzon, who, along with co-workers, has carefully studied the EL spectra of such units and compared them with photoluminescence spectra.[65] The labeling of the various lines given in Table IV follows the discussion of Gershenzon, Mikulyak, Logan, and Foy,[65] and was obtained by comparison of our spectra with the similar 78°K spectra of their Fig. 8.

The notation for the 80°K lines of Table IV is as follows: EE signifies edge emission and is ascribed to recombination at widely separated donor-acceptor pairs.[65,66] It is associated with the sharp-line pair-spectra which appear at higher energies. The *A* line has been ascribed to annihilation of an exciton bound to an impurity.[65,67] The other four low-temperature lines are replications of the EE and A emissions at lower energies due to the simultaneous emission of phonons, acoustic (Ac), or longitudinal optical (LO). The edge emission lines saturate at higher currents while the A lines do not. The room temperature emission is either band-to-band or involves very shallow states.

Although the results for the weakest lines listed in Table IV are relatively less certain than the others, all yield about the same pressure coefficient. The consensus value for $\partial h\nu/\partial P$ is $-(1.1\pm0.1)\times10^{-6}$ eV/bar, in agreement with the band gap coefficient obtained in Sec. 3 from the absorption edge data. The room temperature datum of Table IV provided the lowest energy point shown in Fig. 6. We found no appreciable effect of pressure on the intensity of any of the lines.

The validity of equating the pressure coefficients of these emission lines with $\partial E_G/\partial P$ depends only on the assumption that the transitions involved are between shallow states derived from the band edges, which seems reasonable since their energies lie so close to E_G. However, it has been suggested that the A lines are due to a direct exciton (derived from the valence and conduction band states at $k=0$) strongly bound to an impurity, and that they accidentally occur at an energy near E_G because of a large binding energy. If this were so, then their pressure coefficient should be close to $\partial E_0/\partial P=+11\times10^{-6}$ eV/bar, rather than to $\partial E_G/\partial P=-1\times10^{-6}$ eV/bar. Table IV shows that the reverse is true. Thus, provided that we have correctly identified these lines as belonging to the A complex of Refs. 65 and 67, the mechanism for the A lines more probably involves an ordinary indirect exciton.

We have also measured, at room temperature, the effect of pressure on the broad emission band (width about 0.2 eV) appearing at 1.8 eV. This red emission has been attributed to radiative transitions from a deep donor level, associated with the presence of oxygen in the crystal,[56] to the valence band. The pressure coefficient is $+(1.0\pm0.5)\times10^{-6}$ eV/bar. This coefficient is slightly surprising; it is opposite in sign to $\partial E_G/\partial P$. [In silicon it was found that the pressure coefficient of the energy separation between a deep level and either band edge was a fraction of the (negative) band gap coefficient.[26]] This result implies that the donor binding energy decreases more rapidly with pressure than the band gap.

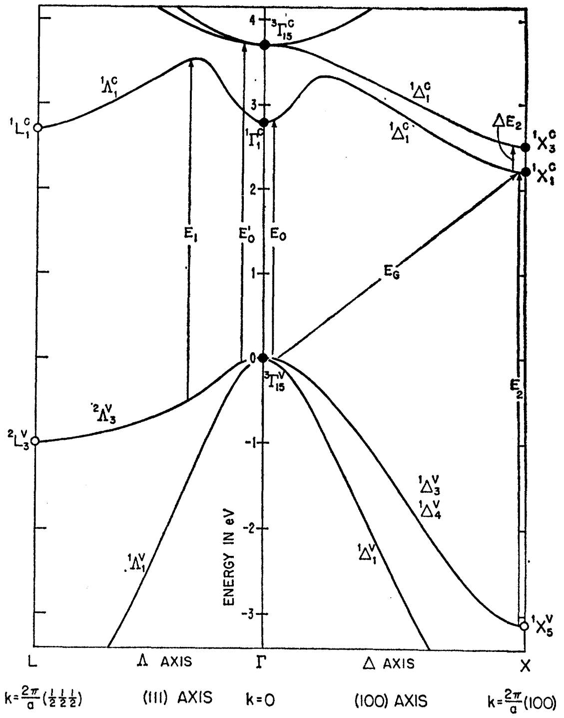

FIG. 12. Band structure of GaP. The states are labeled using the notation for the irreducible representations of the single group of the zincblende lattice. The left-hand superscript appended to each symbol gives the orbital degeneracy of the state. The arrows represent transitions observed in optical experiments. The five energy levels marked by solid circles were those studied by means of our pressure experiments.

7. THE BAND STRUCTURE AND ITS PRESSURE DEPENDENCE

In Fig. 12 we have constructed an electronic energy band diagram for GaP based upon available experimental information. The five energy levels marked by the solid circles are those upon which our pressure experiments bear. The three marked by open circles are from other data discussed below, the *L*-point levels being relatively uncertain. The levels at the symmetry points have been connected by plausible smooth curves which, although somewhat arbitrary, are consistent with various band structure calculations on similar semiconductors, as well as such considerations as crossing or noncrossing of bands and relative magnitudes of effective masses. We have neglected the spin-orbit splitting of valence band levels, which for GaP is about 0.1 eV. Since we do not consider effects of the electron spin, we have labeled the states with the irreducible representations for the single group, rather than for the double group, of the zincblende structure.[6]

The arrows shown in the figure represent the transitions which have been observed in optical experiments,

TABLE V. Effect of pressure on the band structure of GaP.

Transition	E in eV	$\frac{\partial E}{\partial P}$ in 10^{-6} eV/bar	Measurement
$\Gamma_{15}^{v}\rightarrow X_1^{c}$	$E_G=2.22$	$-(1.1\pm 10\%)$	absorption edge,[a] recombination radiation[b]
$\Gamma_{15}^{v}\rightarrow \Gamma_1^{c}$	$E_0=2.78$	$+(10.7\pm 10\%)$	absorption edge,[c] reflectivity peak[d]
$\Gamma_{15}^{v}\rightarrow \Gamma_{15}^{c}$	$E_0'=3.71$	$+(5.8\pm 10\%)$	reflectivity peak[e]
$X_1^{c}\rightarrow X_3^{c}$	$\Delta E_2=0.3$	$+(1\pm 50\%)$	absorption band[f]
$X_5^{v}\rightarrow X_1^{c}$	$E_2=5.3$	$+(2.9\pm 20\%)$[g]	...

[a] See Sec. 3.
[b] See Sec. 6.
[c] See Sec. 3.
[d] See Sec. 5C.
[e] See Sec. 5B.
[f] See Sec. 4.
[g] This is the coefficient for the corresponding transition is silicon, as measured by means of the 4.3 eV silicon reflectivity peak (see Ref. 8).

We have labeled them by their energies. Listed in ascending order of energy, they are as follows:

(1) ΔE_2 is responsible for the infrared absorption in n-type material discussed in Sec. 4;

(2) E_G is the indirect energy gap discussed in Secs. 3 and 6;

(3) E_0 is the direct energy gap discussed in Secs. 3 and 5C;

(4) E_0' is responsible for the reflectivity peak discussed in Sec. 5B;

(5) E_1 is the Λ-point transition, hidden under E_0', discussed in Sec. 5B;

(6) E_2 is responsible for the 5.3-eV reflectivity peak mentioned in Sec. 5A.

In this work, we have studied the effect of pressure on (1) through (4).

The values of E_G, E_0, E_0', E_2, and ΔE_2, are sufficient to fix the energies (relative to ${}^3\Gamma_{15}^{v}$, the valence band maximum) of ${}^1X_1^{c}$, ${}^1\Gamma_1^{c}$, ${}^3\Gamma_{15}^{c}$, ${}^2X_5^{v}$, and ${}^1X_3^{c}$, respectively. To estimate the energies of ${}^1L_1^{c}$ and ${}^2L_3^{v}$, we made use of the following assumptions:

(1) E_1 is equal to E_0' (E_0' is the stronger transition which prevents E_1 from being seen);

(2) the separation of the two bands at L is not very different from E_1 (true for Ge[16]);

(3) ${}^2L_3^{v}$ is about 1 eV lower than ${}^3\Gamma_{15}^{v}$. (The known values of E_0, E_1, and the relative energy of the Γ and X conduction band minima, put the $\Gamma-L$ valence band width at 1.1 eV in GaSb, 1.5 eV in Ge.[7])

The two L-point energies shown in Fig. 12 are then specified. In view of the assumptions needed for their computation, they are clearly much less certain than the other levels.

The right-hand side of Fig. 12 is very similar to a band structure which has been calculated for AlP.[17] AlP is the 3–5 compound which is isoelectronic with Si. This points up the fact that GaP more closely resembles Si than it does Ge. Calculations on Ge-Si alloys[68] show that it is the silicon-rich alloys which most closely correspond to the GaP band structure of Fig. 12.

Our experiments determined the effect of pressure on E_G (Secs. 3, 6), E_0 (Secs. 3, 5C), E_0' (Sec. 5B), and ΔE_2 (Sec. 4). The pressure coefficients are listed in Table V. We have also listed a value for $\partial E_2/\partial P$. This is the pressure coefficient, as measured by us, for the corresponding peak in Si (at 4.3 eV).[8]

In the discussion of Sec. 3 on the pressure dependence of the indirect edge, we defined a quantity $(d/dh\nu)(\partial h\nu/\partial P)_\alpha=\beta$. The measured value of β, obtained from the slope of the linear, low-energy region of Fig. 6, was 1.15×10^{-5} bar^{-1}. We can now compare this experimental result with a theoretical estimate of β based, under certain assumptions, upon the information given in Table V.

In Sec. 3, we showed that β is equal to $-(1/A)\times(\partial A/\partial P)$, where A is the proportionality factor of Eq. (4). In the second-order perturbation theory used in dealing with indirect transitions, it is shown that the oscillator strength for this process [given by the coefficients $C_i^{\pm}$ of Eq. (2), C of Eq. (3), and A^2 of Eq. (4)] is proportional to a term of the form

$$\left(\sum_j \frac{p_j}{E_j}\right)^2;$$

p_j is a matrix element and E_j is an energy denominator corresponding to a virtual two-step process involving a particular intermediate state, specified by j.[69] The pressure dependence of this term is dominated by the pressure dependence of the energy denominators. If we assume, for lack of better information, that all of the p_j's are equal, it follows that $A=\mathrm{const}\cdot\sum_j E_j^{-1}$. Substituting this into the expression for β, we find that

$$\beta=\frac{\sum_j(1/E_j^2)(\partial E_j/\partial P)}{\sum_j 1/E_j}. \tag{7}$$

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[68] F. Bassani and D. Brust, Phys. Rev. 131, 1524 (1963).

[69] We have assumed that phonon energies are negligible relative to the energy separations of electron states ($k\theta_i \ll E_j$ for all i, j). Otherwise E_j^{i} would depend on a phonon energy (specified by i), as well as on the energy of the intermediate electronic state (specified by j). The expression for $C_i^{\pm}$ would then just contain E_j^{i} in place of E_j, but the situation for C and A^2 would be more complicated.

In Fig. 12 there are four intermediate states available for the indirect transition labeled by E_G: ${}^1\Gamma_1{}^c$, ${}^3\Gamma_{15}{}^c$, ${}^1X_3{}^c$, and ${}^2X_5{}^v$. The corresponding energy denominators are E_0-E_G, $E_0'-E_G$, $E_G+\Delta E_2$, and E_2-E_G, respectively. Using (7) and the information given in Table V (and ignoring all other intermediate states but the ones lying within the energy range of Fig. 12), we obtain $\beta=1.0\times10^{-5}$ bar^{-1}. The excellent agreement with the experimental value of 1.15×10^{-5} bar^{-1} is most likely fortuitous in view of the drastic assumptions made; nevertheless, it does show that the measured β is consistent with the proposed pressure-dependent band structure of Fig. 12 and Table V.

8. SUMMARY

The effect of pressure on several optical properties of GaP has been used to construct a tentative electronic energy-band structure for this material over a region of energy within about 4 eV of the valence band maximum at $k=0$. The major experimental results are summarized in Table V; the deduced band structure is shown in Fig. 12.

The data of Table V are consistent with the idea of correlation between pressure coefficients and types of electronic transitions[4–6]: The coefficients of E_G and E_0' are close to those for the corresponding transitions in Si[2,26]; that of E_0 is close to the corresponding coefficient in Ge[10] and GaAs.[11] The result for E_G confirms the location of the lowest conduction band minima as lying along [100] directions in k space.

Evidence for the direct gap E_0 comes from absorption measurements at lower energies, as well as from the weak reflectivity peak at about 2.78 eV, which has not been previously reported. Its temperature coefficient is about -4.6×10^{-4} eV/°K, compared to about -5.2×10^{-4} eV/°K for the indirect gap.

The small pressure shift of the 0.3-eV absorption band observed in n-type material indicates that vertical transitions between conduction bands is the mechanism responsible, as previously proposed by one of the authors.

All of the narrow edge emission lines we observed from a green-emitting diode shifted with pressure at the rate of the indirect gap.

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We are indebted to several laboratories for generously supplying us with the GaP material used in this study. Most of the absorption edge measurements were performed on samples cut from a large polycrystalline ingot provided by J. W. Allen of S.E.R.L., who also provided us with two red-emitting diodes. M. Gershenzon of Bell Laboratories sent us the two green-emitting diodes studied at 80°K. W. G. Spitzer provided us with the n-type material which exhibited the infrared absorption band. Other material was received from the Monsanto Chemical Company, Battelle Memorial Institute, and RCA Research Laboratory.

We are grateful to Dr. Allen, Dr. Gershenzon, and Dr. Spitzer for sending us preprints of their own interesting work, and to Dr. M. Cardona of RCA for valuable discussions. We have also benefited from discussions with P. Grant and V. Prakash of this laboratory.

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