

Effect of pressure on the optical absorption in GaP and $\text{Ga}_x\text{In}_{1-x}\text{P}$ ($x = 0.36$ and 0.5)

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The pressure dependence of the fundamental gaps of GaP and of the two alloys $\text{Ga}_x\text{In}_{1-x}\text{P}$ ($x = 0.36$ and 0.5) has been determined from optical-absorption measurements up to 13 GPa ($T = 300$ K). The pressure coefficients of the lowest direct band gap ($\Gamma_{8v}-\Gamma_{6c}$) in the alloys are nearly identical to that of GaP. For the alloys we find a crossover from direct to indirect ($\Gamma_{8v}-X_{6c}$) fundamental gap at 5.0 GPa ($x = 0.36$) and 2.7 GPa ($x = 0.5$). Phase-transition pressures for the alloys are 15.0 GPa (for $X = 0.36$) and 17.0 GPa (for $x = 0.5$). A quantitative study of the strength of the indirect absorption reveals a strong enhancement with pressure or increasing direct energy gap relative to the effect estimated for $\Gamma \rightarrow X$ transitions within the parabolic-band approximation of the Hartman model. The excitonic character of the virtual direct transition involved in the indirect absorption process does not account for the magnitude of this effect. We suggest that an additional enhancement arises from the nonparabolic nature of the conduction-band dispersion for \mathbf{k} vectors outside the immediate vicinity of the zone center.

I. INTRODUCTION

A recurring scheme for the pressure dependence of the fundamental band gaps of zinc-blende-type III-V compound semiconductors has emerged from a large body of experimental^{1,2} and theoretical³ investigations: The lowest direct energy gap E_0 involving valence- and conduction-band states at the Brillouin-zone center ($\Gamma_{8v} \rightarrow \Gamma_{6c}$) increases with pressure at a typical rate of ~ 0.1 eV/GPa. The energy gap $E_{\Gamma-X}$ for indirect phonon-assisted transitions to excited states near the X point at the zone boundary ($\Gamma_{8v} \rightarrow X_{6c}$) decreases with pressure at a rate roughly 10 times smaller compared with the increase of the E_0 transitions. As a consequence, for compounds with a direct fundamental gap at ambient conditions, one expects a crossover to indirect behavior at some pressure P_c , provided that the zinc-blende-type structure remains the stable phase up to this pressure. The absorption coefficient of indirect transitions is typically 2 orders of magnitude smaller compared with that of direct transitions. Therefore, in direct-gap materials it is only beyond the pressure-induced crossover that the effect of pressure on indirect transition can be investigated by optical methods.

A typical example is GaAs,⁴⁻⁷ where the direct-indirect crossover occurs at about 4.2 GPa. Recently, we have reported⁷ optical-absorption measurements for GaAs near the fundamental gap, with some emphasis on a detailed investigation of the *strength* of the direct as well as the indirect optical transitions under pressure. For the direct gap we have found a linear increase of the transition strength with increasing energy gap, as is expected due to the excitonic character of the direct transition⁸ and in view of similar observations for germanium under pressure.⁹ Furthermore, the indirect absorption in GaAs is also strongly enhanced with increasing pressure. A possible, at least partial, origin of this enhancement

has been attributed⁷ to the increasing strength of the direct excitonic transition, which is involved as an intermediate virtual step in the indirect absorption process.^{10,11}

The primary motivation for the present high-pressure investigation¹² of the optical absorption in the $\text{Ga}_x\text{In}_{1-x}\text{P}$ system was to find out if a pressure-induced enhancement of the indirect absorption is a common feature of other III-V compound semiconductors with similar band structure. The $\text{Ga}_x\text{In}_{1-x}\text{P}$ system is particularly suitable for this study because at ambient pressure these materials have an indirect gap or are close to indirect behavior over a wide range of concentrations,^{2,13,14} as is shown in Fig. 1. Furthermore, these materials exhibit a relatively large change of the direct-gap energy with alloy concentration [from 1.36 eV ($x = 0$) to 2.75 eV ($x = 1$)]. This is expected to result in a large variation of the transition strength for direct excitations across the E_0 gap which would help to elucidate the role of the virtual direct transitions in the indirect absorption process.

Previous high-pressure transport and optical studies of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ system have mainly been concerned with band gaps and their pressure shifts in GaP (Ref. 15) and InP.¹⁶⁻²¹ Transport properties of Ga-In-P diodes under pressure have been investigated by Hakki *et al.*¹⁴ Very recently, a photoluminescence study has been reported for several $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys.²²

In this paper we report the pressure dependence of the direct (E_0) and indirect ($E_{\Gamma-X}$) optical-absorption edges in $\text{Ga}_x\text{In}_{1-x}\text{P}$ with $x = 0.5$ and 0.36 and also of the indirect absorption edge in GaP; furthermore, we report the effect of pressure on the strength of the indirect optical absorption in all three materials. The present experiments were performed in the pressure range 0–13 GPa at 300 K. The two $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys become indirect semiconductors at 5.0 GPa ($x = 0.36$) and 2.7 GPa ($x = 0.5$). The strength of the indirect absorption in $\text{Ga}_x\text{In}_{1-x}\text{P}$ is

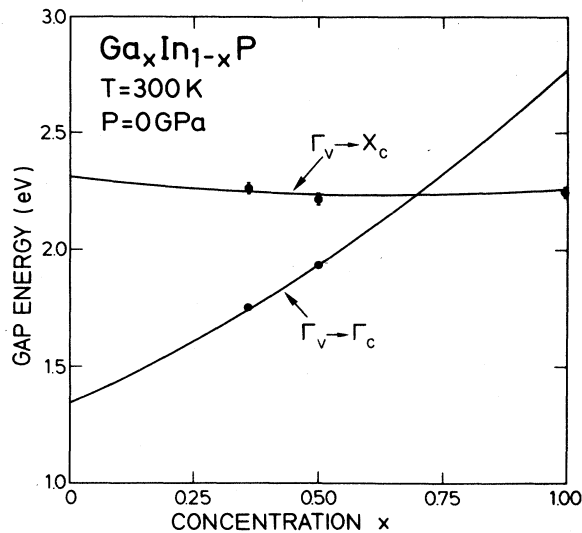


FIG. 1. Direct- and indirect-gap energies of Ga_xIn_{1-x}P at ambient pressure ($T=300$ K) as a function of concentration x . Solid lines are drawn according to band gaps and bowing parameters compiled in Ref. 2. Solid dots represent present experimental results.

found to exhibit a pronounced increase with pressure similar to the earlier results for GaAs. However, the effect is stronger than expected for an excitonic mechanism. We suggest that an additional enhancement of the $\Gamma \rightarrow X$ indirect absorption arises from the nonparabolicity of the conduction-band dispersion for \mathbf{k} vectors outside the immediate vicinity of the Γ point. This nonparabolicity becomes more important with increasing pressure, because the \mathbf{k} -space region for virtual direct transitions increases as the energy separation between the direct and indirect gap increases.

II. EXPERIMENTAL DETAILS

Optical-absorption spectra were measured at 300 K by using a diamond-window high-pressure cell²³ in combination with a micro-optical system. Pressures were determined from the red shift of the ruby luminescence.²⁴ Samples were illuminated with a broadband conventional light source focused to a spot of 40 μm in diameter at the sample position. The transmitted light was passed through a 0.3-m double monochromator (dispersion 1.5 nm/mm) and detected by using fast photon-counting techniques. Optical-absorption coefficients $\alpha(\omega)$ were determined according to

$$\alpha(\omega) = (1/d) \ln[I_0(\omega)/I(\omega)], \quad (1)$$

where $I(\omega)$ is the intensity transmitted through the sample of thickness d at photon energy $\hbar\omega$, and $I_0(\omega)$ is the reference intensity measured through the cell next to the sample. Equation (1) neglects sample reflectivity and thus leads to a nonvanishing value of $\alpha(\omega)$ in the region of transparency which is of no significance here. The samples were mechanically polished down to a thickness

of 50 μm for indirect absorption measurements and to about 5 μm for the direct absorption. As a pressure medium we used either a 4:1 methanol-ethanol mixture or xenon, with equivalent results except for the sample behavior above ~ 11 GPa (see below).

III. RESULTS AND DISCUSSION

A. Pressure dependence of band gaps

Some representative absorption spectra of Ga_{0.5}In_{0.5}P at different pressures are shown in Fig. 2 for samples of 5- μm thickness. Similar spectra were recorded for $x=0.36$. Since no corrections have been applied for reflection losses at the sample surfaces, there is a small zero offset in the spectra of Fig. 2. The maximum detectable absorption level is partly limited by scattered light due to multiple reflections inside the pressure cell. For samples of the given thickness it was not possible to measure spectra beyond the excitonic peak of the direct absorption edge, where a plateau at a level of $\alpha \sim 3 \times 10^4 \text{ cm}^{-1}$ is expected in the frequency dependence of $\alpha(\omega)$ similar to the case of GaAs.²⁵ Thus, we take the kink in the absorption edges, indicated by arrows in Fig. 2, to determine the change of the direct-gap energy E_0 with pressure. The possible error introduced for the absolute values of E_0 would be a small offset to lower energies. The gap energies for zero pressure, however, are in good agreement with those reported elsewhere.²

Experimental results for the pressure dependence of the E_0 gap for $x=0.36$ and 0.5 are shown in Fig. 3. Lines through the data points correspond to the results of a least-squares fit using a quadratic dependence of E_0 on pressure P . The linear and quadratic pressure coefficients are listed in Table I together with coefficients from other absorption measurements and recent theoretical calculations for GaP (Ref. 26) and InP.²⁷ We note from Table I, that the linear and quadratic coefficients for the two alloys are almost identical to the experimental data for GaP; the linear coefficients reported for the direct ab-

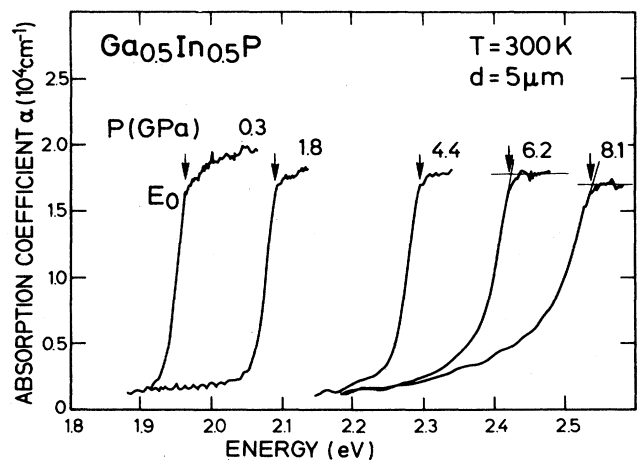


FIG. 2. Absorption spectra of 5- μm -thick sample of Ga_{0.5}In_{0.5}P at different pressures ($T=300$ K). Arrows indicate the energy attributed to the direct band gap.

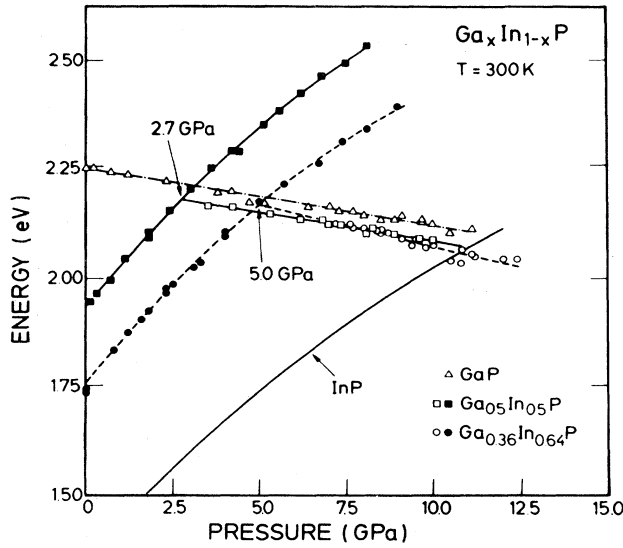


FIG. 3. Direct band gap $\Gamma_{8v} \rightarrow \Gamma_{6c}$ (solid symbols) and indirect gap $\Gamma_{8v} \rightarrow X_{6c}$ (open symbols) of $\text{Ga}_x\text{In}_{1-x}\text{P}$ for $x = 1, 0.5,$ and 0.36 as a function of pressure. The lines represent the results of least-squares fits to the experimental data using quadratic and linear functions, respectively. The data for the direct gap of InP are taken from Ref. 17.

sorption edge in InP (Refs. 17 and 19) are slightly lower compared with the present data for the alloys. Also, photoluminescence studies of InP (Refs. 18, 20, and 21) at various temperatures yield consistently lower pressure shifts (75–85 meV/GPa) of the direct gap.

The relation between energy gap E_0 at ambient pressure and concentration x shows a bowing (see Fig. 1). The pressure coefficients for the four compounds are consistent with a decrease of the “bowing” parameter under pressure, by about 30% at 10 GPa.

Measurements of the *indirect* absorption were performed for GaP and the two alloys using samples of $\sim 50 \mu\text{m}$ thickness. Some representative spectra, again for $x = 0.5$, are shown in Fig. 4. The absorption coefficient

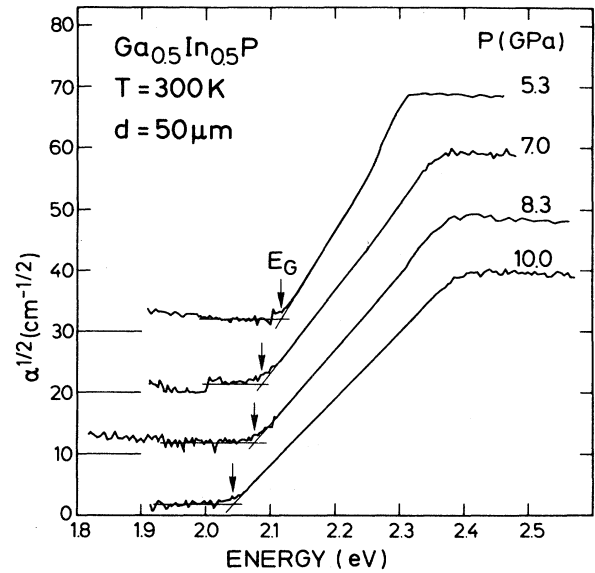


FIG. 4. Square root of the absorption coefficient vs photon energy of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ ($d = 50 \mu\text{m}$) for several pressures. The arrows indicate the onset of absorption, i.e., E_G is the energy of the indirect gap minus the absorbed phonon energy.

$\alpha(\omega)$ for photon energies close to an indirect-gap energy $E_{\Gamma-X}$ (dipole-allowed transition) is approximately given by¹¹

$$\alpha \sim (E_{\Gamma-X} \pm \hbar\Omega_q - \hbar\omega)^2 / [n(\omega)\hbar\omega], \quad (2)$$

if excitonic effects are neglected. Here, Ω_q is the frequency of the emitted (plus sign) or absorbed (minus sign) phonon of wave vector q . The quantity $n(\omega)$ stands for the real part of the refractive index. Thus, we have plotted in Fig. 4 the square root of the absorption coefficient (a constant background was first subtracted) as a function of photon energy. The onset of indirect transitions is determined by the intersection of the two straight lines shown in Fig. 4.

At room temperature the absorption of phonons is as

TABLE I. Data related to the band gaps of $\text{Ga}_x\text{In}_{1-x}\text{P}$ at high pressures: direct gap E_0 at normal pressure and its linear and quadratic pressure coefficients; indirect gap $E_{\Gamma-X}$ at normal pressure, and its linear pressure coefficient. Experimental results are taken from absorption measurements only.

Sample	E_0 (eV)	$E_0(P) = E_0 + bP + cP^2$		$E_{\Gamma-X}(P) = E_{\Gamma-X} + bP$	
		b (10^{-2} eV/GPa)	c (10^{-4} eV/GPa ²)	$E_{\Gamma-X}$ (eV)	b (10^{-2} eV/GPa)
GaP	2.76(1) ^a	9.7(8) ^a	-35(6) ^a	2.25(2)	-1.3(1)
$\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$	1.93(1)	9.56 ^b	-9.16 ^b	2.21(2)	-2.18 ^b
$\text{Ga}_{0.36}\text{In}_{0.64}\text{P}$	1.75(1)	9.7(4)	-29(5)	2.26(3)	-1.3(1)
InP	1.36(1) ^c	9.8(4)	-31(5)	2.31(2) ^c	-1.9(3)
	1.416 ^d	8.4(2) ^c	-18(3) ^c		-3.1(10) ^c
		9.25 ^d	-26 ^d		
		7.8 ^e	-9 ^e		-1.1 ^e

^aReference 15.

^bReference 26 (calculation).

^cReference 17.

^dReference 19 (77 K).

^eReference 27 (calculation).

important as the emission. From symmetry considerations²⁸ the allowed branch for $\Gamma_{8v} \rightarrow X_{6c}$ processes corresponds to longitudinal-acoustic (LA) phonons. Thus, we assign the onset for indirect absorption to the energies $E_G = E_{\Gamma-X} - \hbar\Omega_{LA}$. The LA-phonon energies are about 0.03 eV,² and their pressure dependence can be neglected. The values so obtained for the indirect gaps $E_{\Gamma-X}$ as a function of pressure are also shown in Fig. 3. The lines through the experimental data correspond to a linear relation with zero-pressure energy $E_{\Gamma-X}(P=0)$ and slope $dE_{\Gamma-X}/dP$ obtained from a least-squares fit, as listed in Table I. The absolute value of the slope $dE_{\Gamma-X}/dP$ is slightly higher for the sample with the smallest Ga concentration. We note that the calculated pressure coefficients for the indirect gaps in GaP (Ref. 26) and InP (Ref. 27) is close to the present experimental values.

The pressures P_c at the crossover from direct to indirect band gap are marked by arrows in Fig. 3. The values are

$$P_c = 5.0 \text{ GPa for } x = 0.36$$

and

$$P_c = 2.7 \text{ GPa for } x = 0.50.$$

Furthermore, from Fig. 1 we have $P_c = 0$ GPa for $x = 0.69$. A linear extrapolation of the P_c -versus x curve in Fig. 5 yields $P_c \approx 10.3$ GPa for InP. We note from Fig. 3 that the curves for the indirect gaps cross that for the direct gap of InP at 11.6, 11.0, and 10.7 GPa for $x = 1, 0.5$, and 0.36, respectively. Again, we extrapolate a value of $P_c \approx 10.3$ GPa for InP (see Fig. 5). This value is close to the gap crossover in InP at 10.4 GPa as estimated by Müller *et al.*¹⁷ and also near the lower limit of P_c (10.2 GPa) as given in Refs. 21 and 22. Previous reports^{16,18,19} of a band crossover in InP between 7 and 8 GPa, as detected by Hall-effect, photoluminescence, and optical-absorption studies, are not consistent with our present results.

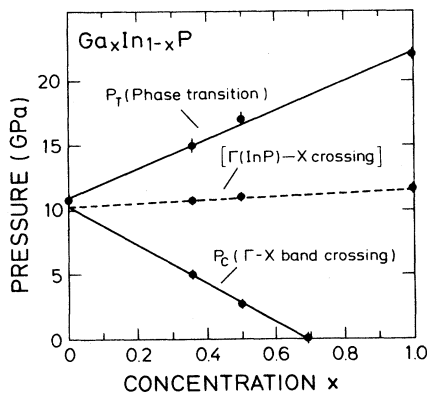


FIG. 5. Pressure P_c for band-edge crossover and pressure P_T for a structural phase transition in Ga_xIn_{1-x}P as a function of concentration x . The dashed line corresponds to the pressure where the indirect band gaps of the alloys and of GaP cross the direct gap for InP in Fig. 3.

The transition to (presumably metallic) high-pressure phases in Ga_xIn_{1-x}P is characterized by an abrupt transformation to an opaque state. The transition pressures P_T of the two alloys and of InP at 300 K, as determined by visual observation of the samples under pressure, are

$$P_T = 10.4(2) \text{ GPa for InP,}$$

$$P_T = 15.0(5) \text{ GPa for } x = 0.36,$$

and

$$P_T = 17.0(5) \text{ GPa for } x = 0.5.$$

Here, P_T of InP refers to a solid-xenon pressure medium, while the other data are for an alcohol mixture medium. Within experimental uncertainty, the value for InP is consistent with other data from optical¹⁷⁻²² and x-ray investigations.²⁹ Using $P_T = 22$ GPa for GaP,³⁰ one finds an almost linear decrease of P_T with increasing concentration of In, as is also shown in Fig. 5. The pressures P_T given in Fig. 5 do not necessarily correspond to the equilibrium transition pressures; usually, a large volume reduction in the order of 15% and a large hysteresis is associated with the first pressure-induced phase transitions of tetrahedrally bonded semiconductors.³⁰ Hence, there may be a significant amount of "superpressing," which depends on the magnitude of nonisotropic stress components acting on the sample. As an example, we note that the corresponding phase transition in GaAs, which is generally accepted to occur at 17–18 GPa in a solid alcohol pressure medium, may be superpressed to 20.5 GPa ($T = 300$ K) in a xenon pressure medium.³¹

It was not possible to measure the indirect gap in the full pressure range between gap crossover and phase-transition pressure P_T . The two alloys as well as GaP turned out to be very sensitive to the formation of light-absorbing or -scattering defects at pressures well below P_T . In transmitted light the samples showed the appearance of dark spots or streaks. In an alcohol mixture this occurred at around 11 GPa; for a xenon pressure medium the limiting pressure was about 13 GPa. Therefore, meaningful indirect absorption spectra could not be measured in the present experiments at pressures above 13 GPa. A possible explanation for the formation of visible defects is that precursor effects of the structural phase transitions build up at crystalline imperfections. The onset of this process appears to depend on the amount of nonisotropic stress. At room temperature a thermal activation may also play a role. In the case of InP, the change of transport properties¹⁶ and the drop in photoluminescence intensity¹⁸ near 6–8 GPa may be related to a similar defect formation. Other possibilities include the crossover of deep impurity levels tied to the X point instead of the band-edge crossover.

B. Strength of the indirect absorption

The approximate energy dependence of the indirect absorption coefficient according to Eq. (2) is no longer valid when the photon energy approaches the higher-lying direct edge. Hartman¹⁰ (see also Refs. 32 and 33) has re-

ported a model for the indirect absorption coefficient which takes into account virtual direct excitations at Γ and uses the parabolic-band approximation for the light- and heavy-hole valence- as well as conduction-band states. Within this model, $\alpha(\omega)$ may be written as

$$\alpha(\omega) = K [A(\omega)]^2 / [n(\omega)\hbar\omega], \quad (3)$$

where K is a constant (in units of eV cm^{-1}) which depends on the momentum matrix elements for electron-photon and electron-phonon interactions, usually assumed to be \mathbf{k} independent, and on light- and heavy-hole masses ($K \sim m_H^{3/2} + m_L^{3/2}$). The dimensionless term $A(\omega)$ accounts for the energy dependence. For the full analytical expression of $A(\omega)$ see, e.g., Ref. 33.

Pressure effects are introduced into this model through the corresponding variation of band parameters, of which the direct-gap energy E_0 is the most important one. The electron and light-hole masses are assumed to vary proportional to E_0 ,^{34,35} and the small decrease of $n(\omega)$ under pressure can be roughly estimated from available experimental data for tetrahedral semiconductors.³⁶ Here, $n(\omega)$ at $P=0$ is taken from Ref. 37 for GaP and from ellipsometric measurements³⁸ for the alloys.

Figure 6 shows the spectral dependence of $\alpha(\omega)$ for a choice of parameters corresponding to a fit to Eq. (3) (solid lines) to the experimental data for GaP at 0.7 and 10.5 GPa. The effect of the direct gap E_0 on the spectral shape is included in the Hartman model. Apart from the divergent behavior of the absorption for photon energies approaching E_0 , the model gives a slightly nonlinear dependence of $\alpha^{1/2}$ near $E_{\Gamma-X}$. The parameter K is found to increase from 8.2×10^5 to 15.7×10^5 eV/cm . On the other hand, within the parabolic-band approximation and

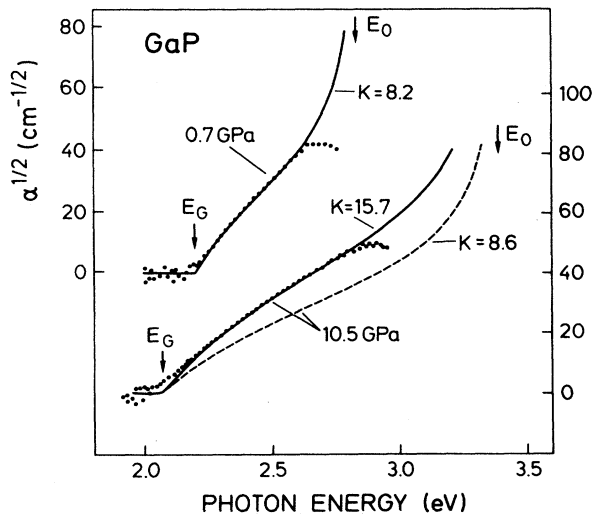


FIG. 6. Square root of the absorption coefficient of GaP at two different pressures (dots) as a function of photon energy. The lines represent the corresponding variation of the spectral dependence according to the Hartman model with the value of the coefficient K [Eq. (3)] given next to them (in units of 10^5 eV/cm). For 10.5 GPa calculations with two values of K (solid and dashed lines) are displayed (see text for more details).

with $K = 8.2 \times 10^5$ eV/cm near ambient pressure, we may estimate K for higher pressures by assuming that the light-hole mass m_L varies proportional to E_0 . In this way, exciton effects and variations of matrix elements are neglected. For GaP at 10.5 GPa we then extrapolate an increase of K by only 5%; the corresponding absorption curve is given by the dashed line in Fig. 6. This absorption is considerably weaker than found experimentally. In fact, for the particular example chosen here, the discrepancy amounts to a factor of 2 in $\alpha(\omega)$.

By fitting Eq. (3) to other experimental spectra for GaP and the two alloys, we obtain K as a function of direct-gap energy E_0 , as shown in Fig. 7, where data for GaAs (Ref. 7) are also included. For all four compounds, one finds a similar systematic increase of K with direct-gap energy E_0 . In the case of GaAs (Ref. 7) this behavior was tentatively explained by considering the excitonic enhancement of the transition probability for direct virtual transitions, which increases linearly with E_0 . However, this effect alone cannot account for the strong increase of K observed for the $\text{Ga}_x\text{In}_{1-x}\text{P}$ system. Moreover, for the $\text{Ga}_x\text{In}_{1-x}\text{P}$ samples K appears to increase roughly proportional to the difference $E_0 - E_{\text{ind}}$ (where E_{ind} is essentially constant for the $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy system). Based on this observation we propose that an additional effect causing an pressure-induced increase of the indirect absorption is due to characteristic properties of the band structure, which depend on the energy separation between the Γ_{6c} and X_{6c} conduction-band states and the related nonparabolic dispersion of the conduction band at \mathbf{k} vectors outside the immediate vicinity of the Γ point.

To illustrate this effect, we make use in Fig. 8 of the band structure of GaAs as calculated by Alouani *et al.*³ at a volume corresponding to an experimental pressure of $P=16$ GPa, where $E_0 - E_{\Gamma-X} \approx 0.9$ eV. The vertical dashed lines indicate the region in \mathbf{k} space where virtual

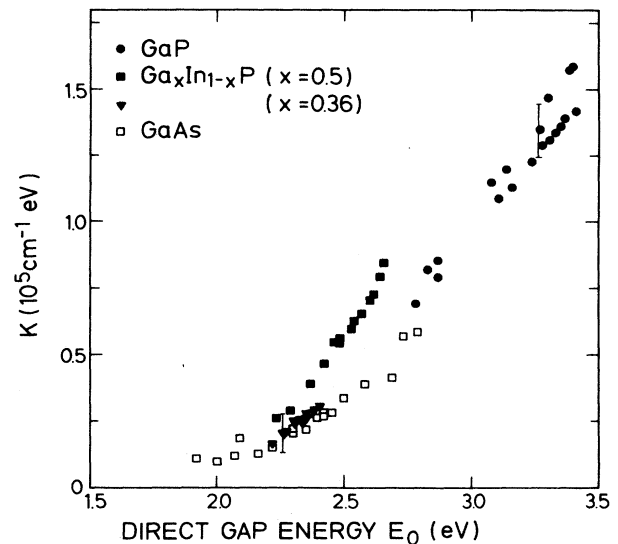


FIG. 7. The absorption strength parameter K of Eq. (3) vs the direct-gap energy E_0 for GaAs, GaP, and $\text{Ga}_x\text{In}_{1-x}\text{P}$ with $x=0.5$ and 0.36 .

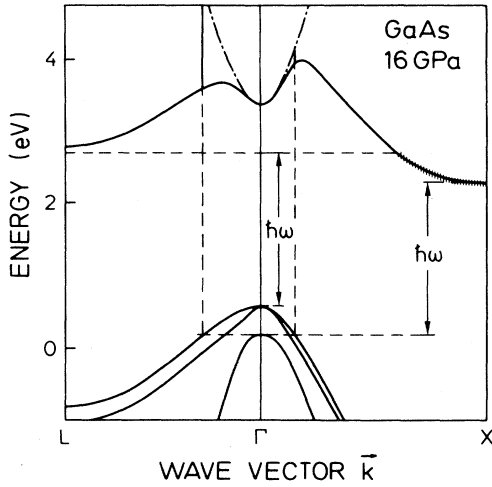


FIG. 8. Band structure of GaAs at 16 GPa from Alouani *et al.* (Ref. 3). The dashed-dotted line corresponds to an extrapolation of the parabolic dispersion of the conduction band according to the effective mass at Γ . The vertical dashed line marks the k -space region of initial states which contribute to indirect Γ - X absorption via virtual excitations of intermediate conduction-band states.

direct transitions contribute to the indirect absorption at a photon energy $E_{\Gamma-X} < \hbar\omega < E_0$. The dashed-dotted line represents the parabolic conduction-band dispersion corresponding to the calculated effective mass at Γ . Obviously, within the relevant region in k space there is a significant nonparabolic contribution to the conduction-band dispersion outside the immediate vicinity of Γ . Thus, at a given k vector the actual energy difference between the valence and conduction band, $E_c(\mathbf{k}) - E_v(\mathbf{k})$, is reduced, which, in particular, affects the energy denominator,

$$D(\hbar\omega) = [E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega]^{-2}, \quad (4)$$

which enters into the calculation of the spectral factor $A(\omega)$.^{10,33} The region in k space near the Γ point which is active for the indirect absorption process increases with the difference $E_0 - E_{\Gamma-X}$; for small energy difference $E_0 - E_{\Gamma-X}$ only transitions near $\mathbf{k} = \mathbf{0}$ are effective and the effect of the nonparabolicity is small. But for higher pressures $E_0 - E_{\Gamma-X}$ is large enough (up to ~ 1.5 eV in GaP) to allow transitions far from Γ , where the nonparabolicity becomes more important.

A rough estimate of the effect of the nonparabolicity on the indirect absorption is obtained by using the band structure of Fig. 8. We integrate the energy denominator Eq. (4) over all final and initial states accessible for direct virtual transitions in the Γ - X direction. For GaAs at 16 GPa the integrated denominator function is larger by a factor of 2 compared to the hypothetical parabolic case. It is obvious from Fig. 8 that a larger value would be obtained for the Γ - L direction. This estimate indicates that the effects introduced by the nonparabolicity of the bands are indeed sufficiently strong to contribute

significantly to the observed enhancement of the indirect absorption. For instance, Fig. 6 shows for GaAs a maximum increase of K by a factor of 6 at $E_0 - E_{\Gamma-X} \approx 0.9$ eV.

Finally, a further increase in K is expected to arise from electron-phonon interaction. In particular, the contribution of phonons other than those with wave vectors near the Brillouin-zone edge could enhance the electron-phonon interaction. However, these effects are more difficult to evaluate or estimate in a quantitative way.

IV. CONCLUSIONS

We have studied the pressure dependence of the lowest direct and indirect gaps of Ga_xIn_{1-x}P ($x = 0.36$ and 0.5) and the indirect gap of GaP by optical-absorption measurements up to 13 GPa. The direct gaps E_0 increase sublinearly with pressure, with an average initial slope of about 98 meV/GPa, while the indirect Γ - X transition energy decreases with pressure, with slopes between -13 and -19 meV/GPa. For the concentrations studied here, the values of the pressure coefficients are not particularly sensitive to alloying and are mainly determined by the anion species. For the alloys we have determined the pressures P_c for crossover from direct to indirect band edge and the pressures P_T of structural phase transitions. From the concentration dependence of P_c and the indirect band gaps we extrapolate a band crossover in InP at 10.3 GPa.

A systematic enhancement with pressure of the *strength* of the indirect absorption was found for all concentrations, relative to predictions of a parabolic band approximation (Hartman model¹⁰) for indirect absorption in tetrahedral semiconductors. These results are in qualitative agreement with previous findings for GaAs under pressure.⁷ The magnitude of the enhancement in the Ga_xIn_{1-x}P compounds cannot be accounted for only by considering the excitonic nature of direct transitions to intermediate virtual states involved in the indirect absorption process. In addition, the perturbing effect arising from the nonparabolicity of the conduction-band dispersion away from the Γ point increases with pressure, because the k -space region for virtual direct transitions involved in the indirect absorption at a given photon energy $E_{\Gamma-X} < \hbar\omega < E_0$ increases with the energy difference $E_0 - E_{\Gamma-X}$. We propose that this mechanism contributes to an enhancement of the probability for indirect transitions. A further enhancement of the indirect Γ - X absorption may be due to the fact that phonons other than zone-boundary phonons participate in the indirect Γ - X absorption.

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