Experimentally, normal Ti^{+3} ions have been observed by paramagnetic resonance.[6] The cation sites closest to the positive ion "core" are in the region of lowest electrostatic energy, and these nearest-neighbor sites will be preferentially occupied at low temperatures. The large dielectric constant in rutile (≈ 150) does not favor the alternate hydrogenic state since the energy is reduced by the factor $1/K_\infty$ and the radial extent of the hydrogenic orbit, being longer than an estimate of the inter-center distance, would give rise to metallic impurity conduction, not observed in rutile.[13]

The observation of electrons hopping to and fro at low temperatures indicates the nature of some of the localized states in reduced rutile, namely polarons localized on cation sites, forming Ti^{+3} ions, in a region of low electrostatic potential adjacent to a positive ion core. Also, the results indicate that consecutive intercationic electron hopping in one direction will be involved at higher temperatures during dc impurity conduction in rutile, and in other similar transition-metal oxides. Dielectric measurements of this type will probably be fruitful in measuring the values of some of the parameters involved in a general treatment of the problem.

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Optical Properties of Gallium Arsenide-Phosphide*

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The index of refraction of $Ga(As_{1-x}P_x)$ is measured as a function of photon energy by the minimum-angle-of-deviation prism method at 300 and 87°K. The dielectric constant in the optical region is found to vary linearly as a function of mole fraction of GaP between the values for GaAs and GaP. Curve-fit data are presented which allow calculation of index of refraction at 300 and 87°K for a given crystal composition x and photon energy. Transmission data on $Ga(As_{1-x}P_x)$ are obtained at 300 and 77°K. The reflectivity is calculated from the index of refraction and is used to calculate the absorption constant, assuming multiple internal reflections in the crystal. In the infrared, true free-carrier absorption is observed for degenerate GaAs-rich mixed crystals, whereas absorption due to transitions from donor levels to the conduction band is dominant in GaP-rich mixed crystals. The band-to-band absorption seen by Spitzer and Whelan in GaAs is observed in GaAs-rich alloys, and is thought to be due to transitions from the (0,0,0) minimum to minima in the $\langle 111 \rangle$ directions. Finally, the absorption edge is investigated, and the Burstein shift of the absorption edge to higher energies with increased doping is observed, as well as shifts to lower energies due to compensation. In all cases, the fundamental absorption edge is found to exhibit an exponential dependence on photon energy.

INTRODUCTION

Very little has been published previously on the optical properties of n-type $Ga(As_{1-x}P_x)$. A few papers[1–4] have given the forbidden energy gap as a function of mole percent GaP. Allen and Hodby[5] have discussed the absorption constant due to the transition from the X_{3v} to the X_{1c} conduction-band minima. Abagyan *et al.*[6] and Chen[7] have given far infrared absorption data for supposedly pure Ga(AsP). Absorption data for GaAs are plentiful,[8–10] as well as for GaP,[11,12] and index-of-refraction data for GaAs[13] and

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GaP [14,15] appear in the literature. In the infrared there are limited index-of-refraction data for phosphorus-rich mixed crystals of Ga(AsP).[6]

This paper gives the results of index-of-refraction measurements which were made by the minimum-angle-of-deviation prism method. The present work also investigates the "free-carrier" absorption, the 0.7- to 1.5-eV interconduction-band transition, and the fundamental absorption edge primarily in *n*-type, GaAs-rich Ga(AsP) alloy, i.e., the composition of Ga(AsP) which is useful for laser junctions.

CRYSTAL GROWTH

The optical properties of the Ga(AsP) crystals reported on here may depend considerably on the method of crystal growth, as do the electrical and luminescent properties.[16] The samples of this work were grown by the closed-tube halogen vapor transport method as described in detail earlier.[17] This method of crystal growth is known to yield excellent homogeneity in doping and composition.[16] In the process of growing the GaP source material and then the Ga(AsP), various impurities may enter the crystal. Besides the dopants intentionally added, silicon and oxygen are probably two of the principal impurities which contaminate the crystals. They can enter the vapor system in either the growth of GaP or of Ga(AsP) due to gallium reacting with the quartz walls of the ampule at the temperatures used.[18] Silicon can act as a shallow donor, whose level is about 0.06 eV below the conduction-band edge in GaP.[19] At high concentrations silicon, being amphoteric, may be an acceptor by substituting for arsenic or phosphorus in Ga(AsP) as it does in GaAs [20] and GaP.[21] If it acts as a donor, it probably has little more effect than spreading the impurity bands that exist because of the intentional *n*-type dopant. If silicon provides an acceptor level, the effect will be to compensate slightly an *n*-type sample.

Other impurities can unintentionally enter the system, either from the quartz ampule or from the gallium, arsenic, phosphorous, or donor dopant, or during the various steps used to clean and handle the ampule and raw materials. As discussed below, several samples show the existence of acceptor levels even though no acceptors were intentionally added to the crystals used in this work. This behavior can likely be attributed to Si acceptors.

INDEX OF REFRACTION

Method

For index-of-refraction measurements, wafers of 30-mil thickness were made into prisms. The prism faces were ground to have an apex angle of near 12°. After rough grinding they were polished with Linde C abrasive on a finely ground glass plate. Final polishing was done with Linde A abrasive on a beeswax lap.

The centers of the prism faces were used in the measurements and were flat to within one wavelength of sodium light as measured with an optical flat. Flatness was also measured with the spectrometer autocollimator, the flatness requirement being that the image of the instrument crosshairs be reflected back from the prism surface in focus. These precautions were taken to avoid the lensing effect which can occur with high-refractive-index materials. Scratches on the surface too large to polish out acted only as an aperture in the optical beam, since the beam was parallel at the sample. For these measurements the crystals were mounted over the aperture in the cold finger of a Dewar as described below.

The monochromator and chopper sections of a Cary model 14RI spectrophotometer were used as the light source for the measurements. The wavelength resolution was ordinarily 40 to 80 Å, although 120 Å resolution was used when a stronger source was needed. For infrared measurements a 0.25- by 3-mm lead sulfide detector was mounted on the eyepiece of the divided-circle spectrometer to detect the focused rays. The output signal from a standard PbS bias supply was introduced into a low-pass preamplifier which had a gain of over 100 at the chopper frequency. The amplified signal was then observed on an oscilloscope equipped with a high-gain plug in preamplifier.

A divided-circle Gaertner Student Spectrometer was used to measure prism angles and angles of refraction. The spectrometer slit was placed at the focus of the Cary spectrophotometer, and an adjustable aperture was fixed to the collimator, so that only light passing through the center of its exit lens was used.

The Dewar assembly for cooling of the prism samples was constructed of stainless steel and insulated with Styrofoam, and was mounted on the prism table with polystyrene rods in such a way that it could be moved in order to maintain the sample prism in the center of the light beam as its refractive edge (the intersection of the two refractive faces) was adjusted to be vertical. A large polyethylene jug was cut to enclose the center post supporting the prism mount and the apparatus collimator and telescope lenses. Polyethylene film was used to seal around the top edge of the Dewar and the

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telescope but still allow movement of each. The aperture which masked all but the centers of the collimator lens and crystal was mounted near the crystal. Thus, when the Dewar was removed to measure the angle of the unrefracted rays, only those rays passing through the aperture were measured. For 87°K measurements, the sample space was kept under a positive pressure of gaseous helium to keep condensate from forming on the sample prism. To measure sample temperature, a thermocouple was mounted in a small hole in the cold finger near the sample prism. The prism was mounted with Wakefield Thermal Compound on the Dewar cold finger.

To adjust the prism sample so that the minimum angle of deviation could be measured, the approximate angle of minimum deviation was first determined. The telescope was then set at a slightly lesser angle, so that the signal on the oscilloscope was about 50% of full screen. The prism was then rotated until the signal was maximum. The angle of the refracted ray was determined by averaging the angular positions on either side of maximum signal at which the signal was $\frac{2}{3}$ of maximum. The angle of the unrefracted rays was measured in the same manner with the Dewar removed.

With the Gaertner Student Spectrometer the sample prism apex angle and angle of minimum deviation could be measured to closer than 1′ of arc. This led to a calculated worst-case error in index of refraction of less than ± 0.006 due to error in prism apex measurement, and ± 0.002 due to error in measurement of the angle of the refracted ray. The prism angle could easily be set to within 1°. This led to a calculated possible error of $+0.0015$. Thus, the maximum total error could be $+0.0095$ to -0.0065 or about $+0.3\%$ to -0.2%.

Results and Discussion

Figure 1 shows the index of refraction at 300°K as a function of photon energy for GaAs and GaP, and for Ga(AsP) of a number of different values of mole percent phosphorus. Figure 2 shows the results of measurements at 87°K. The solid curves are calculated from the equation[13]

$$n^2 = A + B\lambda^2/(\lambda^2 - C), \qquad (1)$$

with the photon wavelength λ expressed in microns and the equations for A, B, and C given in Table I. With the parameters of Table I, Eq. (1) fits the experimental points to within 0.009 for all values of crystal composition x except $x=0.125$, which seems to be a spurious point as discussed below. This is within the maximum experimental error.

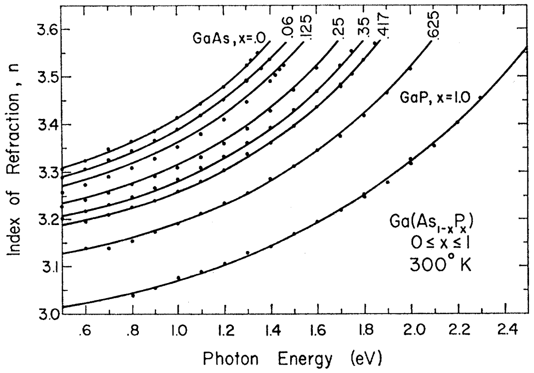


FIG. 1. Index of refraction of Ga(AsP) at 300°K as a function of photon energy for several values of mole fraction GaP. Solid lines are the result of curve fitting.

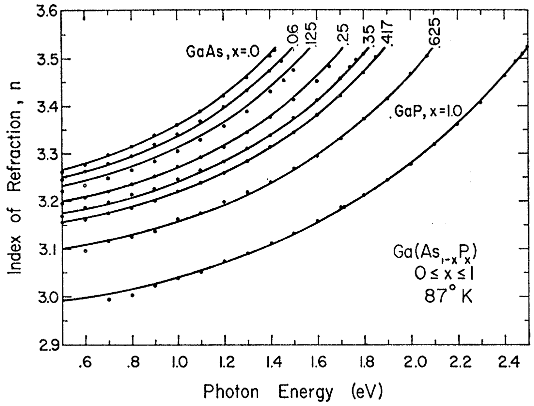


FIG. 2. Index of refraction of Ga(AsP) at 87°K as a function of photon energy for several values of mole fraction GaP. Solid lines are the result of curve fitting.

The curves in each case were cut off at low photon energies either by the long-wavelength cutoff of the lead sulfide detector or by high free-carrier absorption in the crystal, and at high photon energies by the large band-gap absorption. Measurements were made by eye from 1.7 eV to the band gap in samples of more than 0.25 mole fraction GaP. In these cases the plotted curves turn upward more, inasmuch as the eye served as a more sensitive detector than the electronic instrumentation used, and thus allow measurement more closely to the band-gap edge. Because of the homogeneity of the samples, the slit image always appeared sharp and was spread very little when the refracted rays were observed visually.

The formulas of Table I were obtained by fitting the experimental points for each x with Eq. (1) after the method of Marple and Kreiger.[13] The values of the parameters for the best curve fit for each crystal

TABLE I. Curve-fit parameters for refractive index $n^2=A+B\lambda^2/(\lambda^2-C)$ as a function of x for Ga($As_{1-x}P_x$).

300°K

$A=4.1189+4.0625x-10.3446x^2+2.7809x^3$

$B=6.6369-5.8747x+10.6049x^2-2.9874$

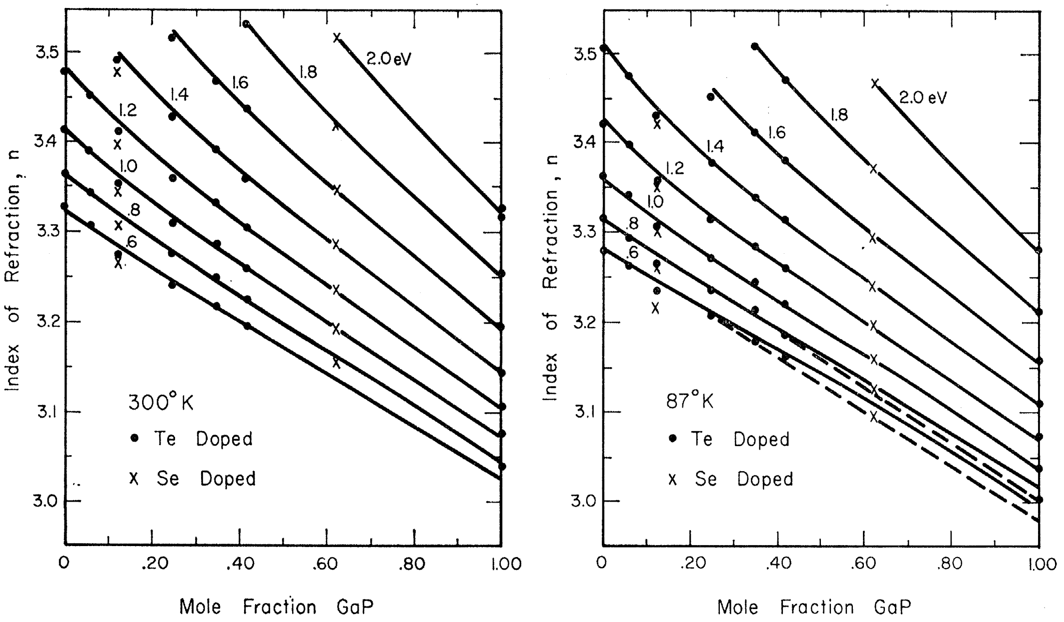
$C=[1.23978/(2.9025+0.5088x+1.1201x^2)]^2$

87°K

$A=5.3551+2.1630x-7.8548x^2+2.5740x^3$

$B=5.1470-3.7008x+7.8490x^2-2.6754x^3$

$C=[1.23978/(2.7402+0.8356x+0.6544x^2)]^2$



(a) (b)

FIG. 3. (a) Index of refraction of Ga(AsP) at 300°K as a function of mole fraction GaP for constant values of photon energy. (b) Index of refraction of Ga(AsP) at 87°K as a function of mole fraction GaP for constant values of photon energy.

composition x are shown in Table II, along with the high-frequency dielectric constant $\epsilon_\infty = A+B$ (in contrast to frequencies below the reststrahlen frequencies) and the maximum error of the fit. The square root of C is the wavelength λ_0 of the classical oscillator, and the peak of absorption is at the classical oscillator frequency $\omega_0 = 2\pi c/\lambda_0$, where c is the speed of light. Since the energies of the lowest band gap of Ga(AsP) and higher-energy subsidiary gaps are roughly linear with crystal composition x,[22,23] the energy $1.24/\lambda_0 = 1.24/\sqrt{C}$ should be nearly linear with x. However, the constant C obtained by curve fitting depends strongly on how much the index of refraction turns upward near the band gap. Thus, for the samples in which measurements in the visible could be made, the constant C is relatively lower and the energy $1.24/\sqrt{C}$ is higher. Hence, the curve of $1.24/\sqrt{C}$ as a function of crystal composition x bends upward for higher x values. The values of $1.24/\sqrt{C}$ which best fell on a line were least-squares curve fit. Then from the calculated values for C, new values of A and B were calculated, once again by fitting of the experimental points by the least-squares procedure. Finally, the parameters A and B for each x, apart from those for $x=0.125$, were least-squares fit as a function of x to arrive at the equations of Table I.

TABLE II. Curve-fit parameters to fit original data for $\mathrm{Ga(As_{1-x}P_x)}$ for refractive index.

X	A	B	C	ϵ_∞	Maximum error
			300°K		
0.0	4.0518	6.6961	0.1820	10.7479	0.0034
0.06	0.1956	10.4358	0.1182	10.6314	0.0030
0.125	4.2798	6.1803	0.1721	10.4601	0.0034
0.25	4.6599	5.6310	0.1622	10.2909	0.0042
0.35	4.3483	5.8149	0.1486	10.1632	0.0036
0.417	4.1354	5.8977	0.1390	10.0331	0.0030
0.625	0.3963	9.2240	0.0876	9.6203	0.0048
1.00	0.6215	8.3765	0.0749	8.9980	0.0060
			87°K		
0.0	5.2324	5.2620	0.2016	10.4944	0.0050
0.06	1.1506	9.2208	0.1221	10.3714	0.0038
0.125	4.6822	5.5491	0.1699	10.2313	0.0024
0.25	4.3235	5.7631	0.1471	10.0866	0.0036
0.35	5.7007	4.2864	0.1685	9.9871	0.0039
0.417	4.9081	4.9301	0.1473	9.8382	0.0028
0.625	3.9915	5.5152	0.1200	9.5067	0.0036
1.00	2.3234	6.5365	0.0866	8.8599	0.0042

Figures 3(a) and 3(b) show the variation in index of refraction of Ga(AsP) as a function of composition x at constant photon energy. These curves are linear at low energy as has been reported by Abagyan *et al.*[6] The curves turn upward at lower energies for low values of x because here band-gap absorption begins to occur. It is seen that data from both of the $x=0.125$ samples do not fall on the curves at low energy, and data from the selenium-doped sample are lower everywhere. Thus, the value $x=0.125$ was not used in the curve fitting. An $x=0.625$ selenium-doped sample falls on the curve, so that no generalization can be made regarding the

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TABLE III. Summary of the properties of Ga($As_{1-x}P_x$) samples used for absorption measurements.

Sample	x	Dopant	Quality[a]	Carrier conc. (cm^{-3}) 300°K	Mobility (cm^2/V sec) 300°K	Exponential slope (eV^{-1}) 300°K	Carrier conc. (cm^{-3}) 77°K	Mobility (cm^2/V sec) 77°K	Exponential slope (eV^{-1}) 77°K
1	0.06	Te	p	...	...	15.2	...	...	18.8
2	0.125	Te	p	1.76×10^{16}	32.9	13.55	...	...	13.4
3	0.125	Se	s,c	1.04×10^{18}	322	14.8	1.02×10^{18}	368	17.2
4	0.25	Se	v	8.23×10^{17}	298	12.8	1.03×10^{18}	187	10.4
5	0.25	Se	c	1.67×10^{18}	380	9.84	$1.6\ \times10^{18}$	423	12.0
6	0.25	Te	q,c	1.47×10^{18}	713	14.94	1.51×10^{18}	727	12.87
7	0.30	Te	q,c	$7.8\ \times10^{17}$	500	...	$9.6\ \times10^{17}$	473	11.2
8	0.30	Te	pc	$3.9\ \times10^{18}$	680	...	4.15×10^{18}	1060	...
9	0.33	Te	q,c	$5.1\ \times10^{17}$	92.1	10.2	6.37×10^{16}	482	7.78
10	0.33	Te	q,c	$7.7\ \times10^{17}$	624	10.8	1.26×10^{18}	690	10.2
11	0.33	Te	q,c	$1.6\ \times10^{18}$	605	11.0	1.65×10^{18}	915	10.2
12	0.33	Te	cl,p	$2.4\ \times10^{18}$	399	...	2.02×10^{18}	605	6.83
13	0.44	Te	cl,p,v	6.65×10^{17}	146	11.9	5.01×10^{15}	600	...
14	0.50	Te	c	...	...	...	...	...	...
15	0.625	Se	v	...	...	7.22	...	...	7.26
16	0.625	Te	cl,v	1.02×10^{18}	30.4	7.22	9.86×10^{15}	137	8.1

[a] Quality code: s: single crystal, q: quasisingle, p: polycrystalline, c: clear, pc: partly cloudy, cl: cloudy, v: voids.

effects of the type of dopant on index of refraction from these data.

We might expect that even at low values of photon energy the curve of index of refraction as a function of x for constant photon energy would be nonlinear, since there is added absorption due to spin-orbit splitting for x less than 0.50 or 0.60 as deduced from the reflectivity data of Bergstresser *et al.*[22] and Woolley *et al.*[23] In the range of composition x where there is added absorption due to spin-orbit splitting, the index of refraction should be relatively higher than in the $0.5\leq x\leq 1.0$ region, causing nonlinearity in the curve. These measurements, however, show no such nonlinearity due to the small effects expected at low energies, the accuracy of the measurements, and free-carrier effects. When the high-frequency dielectric constants $\epsilon_\infty = A+B$ from Table II are plotted as a function of mole fraction GaP in Ga($As_{1-x}P_x$), along with $A+B$ calculated from the equations of Table I, we see that there is a slight discrepancy between the two plots, but essentially ϵ_∞ varies linearly as a function of mole fraction GaP between the values for GaAs and GaP.

The measurements reported here for GaAs and GaP compare favorably with the measurements of Marple for pure GaAs,[13] of Bond for pure GaP,[15] and of Folberth and Oswald for apparently very impure GaP.[14] The small differences are due to differences in the doping of the crystals. If the effective mass $m^*=0.072m$ for GaAs, from Stern's[24] Eq. (22) the change in index of refraction due to free carriers is

$$\Delta n = -9.6\times10^{-21} N/nE^2, \tag{2}$$

where N = free-carrier density, n = index of refraction, and E = photon energy in electron volts. For a free-carrier density of $N=3.5\times10^{18}$ carriers/cm^3, $E\sim0.7$ eV, and $n=3.1$, Δn is calculated as -0.02. A free-carrier density of $N=3.5\times10^{18}$ carriers/cm^3 is roughly the doping level in the GaAs sample measured, and $\Delta n=-0.02$ is roughly the difference in Marple's data for "pure" GaAs and the present measurements for doped GaAs at a photon energy of 0.7 eV. Similarly, Bond's values for "pure" GaP are somewhat higher than those reported here, and Folberth and Oswald's are slightly lower.

ABSORPTION

Experimental

The crystals used for absorption measurements were mostly polycrystalline with individual crystallites having dimensions of roughly 3 mm. Most were clear and homogeneous appearing when examined in transmission with a strong light. Some, however, were cloudy over part of the area used, and those are noted as cloudy in Table III. Table III shows also crystal quality and doping for each sample.

Previous measurements have indicated that ingots grown in this laboratory are quite homogeneous with regard to doping and mole fraction GaP in Ga(AsP).[16,17] Therefore Hall data probably are accurate for optical samples, although measured on the same ingot but other wafers than those used in the optical measurements reported here. Carrier concentration was calculated from the equation $R=1/ne$, but this must be interpreted with cognizance of the effect of the relative position of the direct and indirect minima on the Hall effect.[25]

The wafers for absorption measurements were prepared by grinding with successively finer compounds to a depth such that work damage from previous saw cuts or grinding was reduced if not eliminated. Polishing was accomplished with Linde C and A abrasives, and

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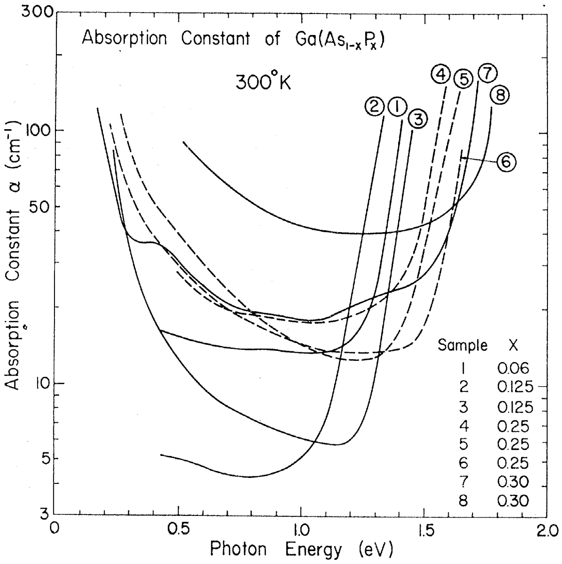

FIG. 4. Absorption data of Ga(As$_{1-x}$P$_x$) at 300°K with mole fraction GaP less than 0.3.

final polishing was performed with Linde B in order to minimize errors in reflection coefficient due to surface scattering.[26] No etch polish was found satisfactory for polycrystalline material, as the chemical activity on different planes caused the wafer thickness to vary from crystallite to crystallite.

A Cary 14RI spectrophotometer with a quartz-iodine lamp was used to measure optical density from 3 μ to the band gap. The resolution was less than 0.004 eV at low values of absorption constant at the band-gap region, and 0.008 eV at the highest absorbance values. Measurements were limited to optical densities of less than about 4.3 because of scattered light. In the infrared a Beckman IR12 was used to measure the percent transmission of the samples. Resolution was typically 0.005 eV, with a maximum of 0.009 eV near 0.25 eV. A single beam "sample-in, sample-out" procedure was used for highest accuracy. The samples were mounted with Wakefield Thermal Compound over the aperture in the cold finger of a liquid-nitrogen Dewar which was pumped to high vacuum continuously during the measurements.

The absorption constant was calculated from the usual formula considering multiple internal reflections,[27] with the reflectivity R calculated from

$$R=(n-1)^2/(n+1)^2\,, \tag{3}$$

with the aid of Eq. (1) and the constants of Table I. A slight inaccuracy occurs in these values of R at 77°K as the index of refraction was measured at 87°K.

Figures 4 and 5 show absorption data of Ga(As$_{1-x}$P$_x$) samples for various values x of mole fraction GaP, at 300°K. Figures 6 and 7 show data for the same crystals at 77°K. All of those for $x\leq 0.33$ are laser-quality crystals. Further data on each sample are shown in Table III.

Free-Carrier Absorption

Figure 8 shows typical absorption spectra for Ga(As$_{1-x}$P$_x$) as redrawn from Figs. 4 through 7. The sharp absorption peak evident at 0.4 eV for $x>0.33$ has been discussed by Allen and Hodby.[5] The broadly peaked band-to-band absorption and band-gap absorption regions are discussed below. For crystal compositions $x\leq 0.50$ the free-carrier absorption constant at 77°K is always less than the absorption constant at 300°K. For $x\geq 0.65$, and probably for $x>0.5$, the low-temperature "free-carrier" absorption constant is greater than the high-temperature absorption constant. The data may be partially explained in terms of the conduction-band properties and impurity levels. The long-wavelength absorption depends on the position of the (0,0,0) and (1,0,0) conduction-band minima relative to each other.

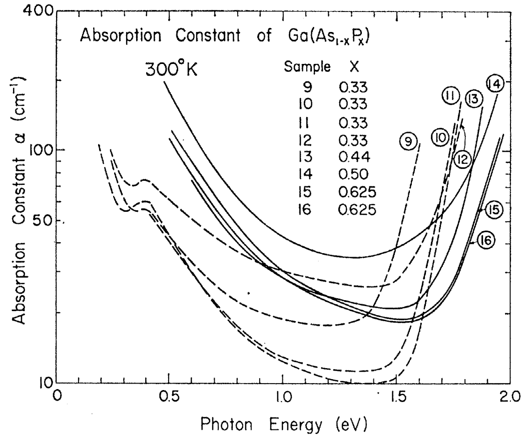

FIG. 5. Absorption data of Ga(As$_{1-x}$P$_x$) at 300°K with mole fraction GaP between 0.33 and 0.625.

From the carrier concentration data of Table III we see that most samples are degenerate as long as the light-mass (0,0,0) conduction-band minimum is lowest, and the samples are nondegenerate when the (1,0,0) minima are lowest. This is due to much greater splitting of the donor energy levels near heavy-mass minima, which leads to a nondegenerate semiconductor when the heavy-mass minima are the lowest.

For $x\leq 0.25$ the (1,0,0) minima are much higher than the (0,0,0) minimum and also the Fermi level, and hence are not occupied by electrons. For $x\leq 0.25$ change in position of the energy level of the (1,0,0) minima with temperature does not affect the number of carriers in either the indirect minima or direct minimum. Since

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[26] H. E. Bennett and J. O. Porteus, J. Opt. Soc. Am. **51**, 123 (1961).

[27] H. Y. Fan and M. Becker, *Symposium Volume of the Reading Conference* (Butterworths Scientific Publications, Ltd., London, 1951), p. 132.

the samples are degenerate, the carrier concentration in the direct minimum is approximately constant with temperature. Thus, true free-carrier absorption is observed which is lower for lower temperature, since there are fewer phonons at lower temperature available for phonon-assisted intraband transitions.

For $0.25 \leq x \leq 0.5$ the (1,0,0) minima and their associated donor levels[28] are low enough at room temperature to cause the (0,0,0) minimum to gain carriers as temperature is lowered and the two different band minima move farther apart. In this case, the free-carrier absorption drops as temperature is lowered, but not as much as if the number of electrons in the (0,0,0) minimum remained constant.

For Ga($As_{1-x}P_x$) crystal composition $x \geq 0.625$ (and probably for $x > 0.5$) the samples are no longer degenerate, and the Fermi level lies between the (1,0,0) conduction-band minima and their associated donor levels. The (1,0,0) minima are lower than the (0,0,0) minimum. At lower temperature, due to the sharpening of the Fermi function, the indirect (1,0,0) donor level is more highly populated than it is at room temperature. This leads to increased absorption due to direct transitions from the donor level to the conduction band and is easily mistaken for free-carrier absorption if the temperature dependence is ignored. Thus, in nondegenerate indirect material the absorption in the long-wavelength range is higher at lower temperatures than it is at higher temperatures because of transitions from the donor level to nearby conduction-band minima. This is seen in Fig. 8 for the sample of composition $x = 0.625$ (after Hodby[29]).

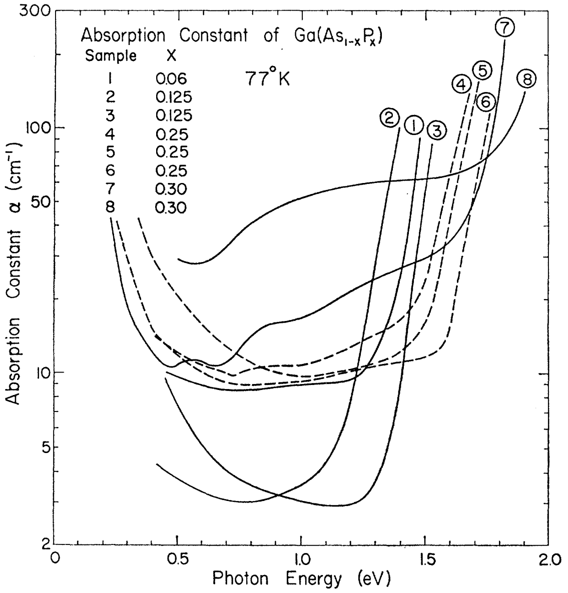

FIG. 6. Absorption data of Ga($As_{1-x}P_x$) at 77°K with mole fraction GaP less than 0.3.

In the infrared, the absorption constant is proportional to λ^n. For the samples of this work (with mole fraction GaP about 0.3) and for the samples measured by Hodby,[29] the exponent n was always greater at 77 than at 300°K. For the GaAs-rich alloys of Ga($As_{1-x}P_x$), where true free-carrier absorption is observed, the change in slope with temperature is probably due to a change in scattering mechanisms. The exponent is small for phonon scattering and larger for impurity scattering. Thus, at low temperature where phonon scattering is less, the high-exponent impurity scattering predominates. This explanation has been given before by Fan *et al.*[30] for Ge and applies here also. It is possible and likely that impurity scattering dominates the behavior of GaP-rich Ga(AsP) also at low temperatures. Although at 77°K most carriers "freeze out" on the donor levels, there are still about 10^{16} carriers per cm^3 in the conduction band.

Of general interest is the magnitude of free-carrier absorption at a given wavelength. The absorption constant is proportional to the number of free carriers, to the number of phonons, and to the impurity scattering centers present. There is also an additional scattering mechanism (alloy scattering) which arises on account of the disorder of the crystal. Chen[7] and also Verleur and Barker[31] have shown that there are GaAs-like and GaP-like optical phonons occurring simultaneously in Ga(AsP). This should also hold true for acoustical phonons. The As and P atoms should act as charged impurity scatterers unless they are perfectly ordered in

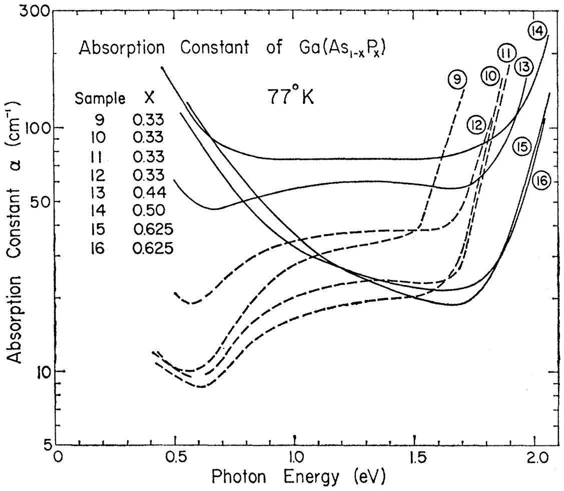

FIG. 7. Absorption data of Ga($As_{1-x}P_x$) at 77°K with mole fraction GaP between 0.33 and 0.625.

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[28] N. Holonyak, Jr., C. J. Nuese, M. D. Sirkis, and G. E. Stillman, Appl. Phys. Letters **8**, 83 (1966).

[29] J. W. Hodby, thesis, Oxford University, 1966, p. 71 (unpublished).

[30] H. Y. Fan, W. Spitzer, and R. J. Collins, Phys. Rev. **101**, 566 (1956).

[31] H. W. Verleur and A. S. Barker, Bull. Am. Phys. Soc. **11**, 72 (1966).

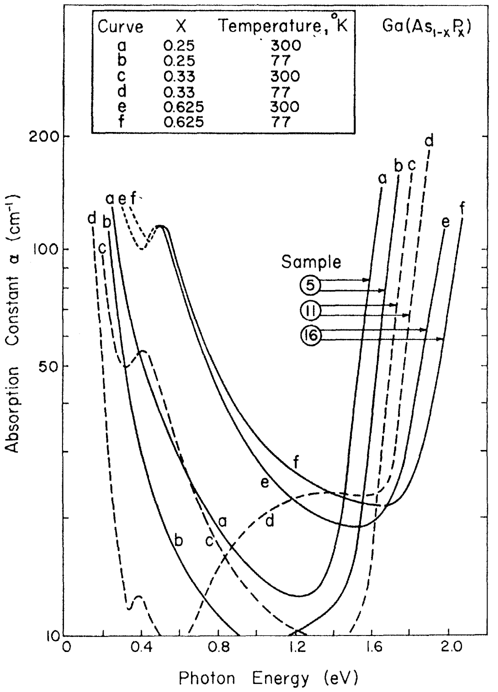

FIG. 8. Typical absorption constant data for Ga(AsP) at 300 and 77°K as a function of photon energy. Free-carrier absorption data for sample 16 is known from other sources.

the lattice, which under ordinary conditions is highly unlikely. Crystal disorder should lead to alloy scattering and matrix elements identical to those which account for the resistance in alloys.[32]

If H_P is the Hamiltonian of a phosphorus atom, H_{As} is the Hamiltonian of an arsenic atom, and there is a fraction x of phosphorus atoms and $(1-x)$ of arsenic atoms constituting the crystal, the total probability of scattering is proportional to the total matrix element squared:

$$M^2 = x(1-x)\left[\int \Psi_{k'}^*(H_P - H_{As})\Psi_k dV\right]^2. \tag{4}$$

The Hamiltonians H_P and H_{As} can contain perturbations due to the various scattering mechanisms outlined above. Hence, there is a first-order effect of each of the various scattering mechanisms, and a second-order effect due to alloy scattering.

Figure 9 shows data taken by Hodby[29] which give the value of the coefficient A when free-carrier absorption is written as $\alpha = A\lambda^n$. The solid line is calculated from $A = 24x(1-x)$ for the 77°K data. The room-temperature data show the same $x(1-x)$ trend but with higher absorption and more scatter. This is still consistent with the fact that "free-carrier" absorption is lower at 300°K since the exponent n is lower. The doping of Hodby's samples is unknown, but the data show a trend which may be interpreted as alloy scattering. Data taken in connection with the present work are all for $x \approx 0.33$ and, because of the lower number of free carriers, fall far below the values predicted by the solid line in Fig. 9. We have noticed, however, that absorption is higher for $x \approx 0.5$. This precluded taking data of free-carrier absorption for $0.44 \leq x \leq 0.625$.

To attempt verification of the theory of alloy scattering, the free-carrier absorption of samples of still higher quality material than presently available (of various compositions) should be measured. The carrier concentration should be as near constant as possible, and particular care should be exercised at points such as $x = 0.5$ to look for ordering which would lower the absorption constant.

Interconduction-Band Transition

In this section we discuss the broad absorption band seen at about 0.4 eV in GaAs and at higher energy in Ga(AsP) alloys (see Figs. 6–8) and present evidence to support Spitzer and Whelan's explanation that the transitions involved have their final state in the (1,1,1) minimum.[8] Experimentally we observe that for $x \leq 0.25$ the absorption constant is always lower at 77°K than it is at 300°K. For $0.3 \leq x \leq 0.5$, the absorption constant in the region of interest is higher at 77 than at 300°K, and the broad peak is quite pronounced. When $x \geq 0.625$, the absorption constant is also higher at 77°K, but the broad peak almost disappears. The data of Spitzer and Whelan[8] for GaAs show that the broad absorption peak is not seen in heavily doped materials. This is probably the reason it is not seen in the curves shown here with mole fraction GaP less than 0.25. Vieland and Kudman[33] have attempted to explain this effect in terms of excess absorption by un-ionized Se or Te.

Figure 10 shows, for various values of composition x, the absorption constants due to interband transitions. These curves were obtained by subtracting the extrapolated free-carrier absorption, and where necessary the extrapolated absorption due to the $X_1 \rightarrow X_3$ transition, from the original curve of absorption constant. We see that the low-energy threshold moves to higher energy with increasing mole fraction GaP, and there is a large

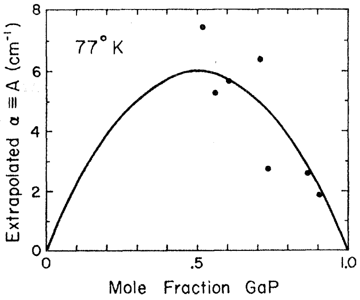

FIG. 9. Value of free-carrier absorption constant of Ga(AsP) extrapolated to 1 μ (77°K).

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[32] N. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 296.

[33] L. J. Vieland and I. Kudman, J. Phys. Chem. Solids **24**, 437 (1963).

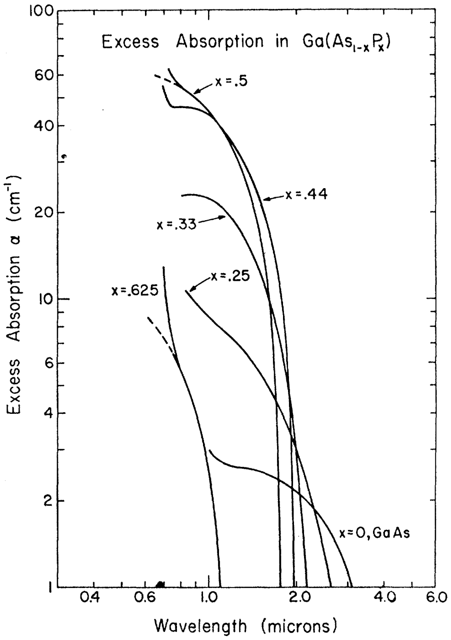

FIG. 10. Excess absorption in $Ga(As_{1-x}P_x)$ at 77°K (due to interconduction-band transitions) as a function of wavelength with mole fraction GaP a parameter.

change in energy and magnitude for $x=0.625$. It might be argued that the apparent thresholds are caused by broad absorption bands at much longer wavelength, which one sees only when free-carrier absorption is slight at short wavelength. The absorption curves for GaAs and for $Ga(As_{0.67}P_{0.33})$ at 77°K, however, show a definite "hump" and therefore provide the most reliable evidence of an absorption threshold near 0.4 to 0.6 eV.

To determine which interband transition causes the broad peak, it is necessary to first determine the initial state of the transition. From the above data for x less than 0.4 or 0.5, it is clear that the initial state is in the (0,0,0) minimum, or possibly the donor level beneath it if the semiconductor is nondegenerate. There is evidence to indicate that the initial state is in the (1,0,0) minima or the indirect donor levels for $x>0.5$. The reasoning is as follows:

1. The absorption constant is proportional to the number of electrons in the initial state.
2. For $x<0.4$ or 0.5, as temperature is lowered the (1,0,0) minima move upward with respect to the (0,0,0) minimum, thus causing any electrons in the (1,0,0) minima or their associated donor levels to move into the (0,0,0) minimum.[28] Thus for $0.3\leq x\leq 0.5$, the (0,0,0) and (1,0,0) minima are close together, and there are more electrons in the (0,0,0) minimum at 77 than at 300°K.
3. For $0.3\leq x\leq 0.5$, the absorption constant is higher at 77 than at 300°K in the interconduction-band transition region.
4. For $x\geq 0.625$, there are very few electrons in the (0,0,0) minimum, most being in the (1,0,0) minima and the indirect donor levels at both 77 and 300°K.
5. Since the absorption constant has the characteristics shown in Fig. 8, and discussed above, and changes in the way the number of electrons in the (0,0,0) minimum changes with x and temperature, we see that for $x<0.4$ or 0.5 the initial state is the (0,0,0) minimum. The evidence that the initial state is the (1,0,0) minima or the indirect donor levels for $x>0.5$ is discussed below. In any case, the initial energy is probably near the Fermi level.

The initial state cannot be a deep level, as it would be at least 0.3 eV below the conduction band and would be occupied at all temperatures, giving a different temperature dependence from that experimentally observed. The final state of the transition is more difficult to specify. Spitzer and Whelan[8] originally guessed that the (1,1,1) minima are the final state, based on Callaway's model for GaAs.[34] Haga and Kimura[35] feel that the (1,0,0) minima are the final state.

Figure 11 shows why Spitzer and Whelan are most likely correct. The energy of the transition, as defined by the energy where the absorption constant of the band-to-band transition is 20% of the maximum, is

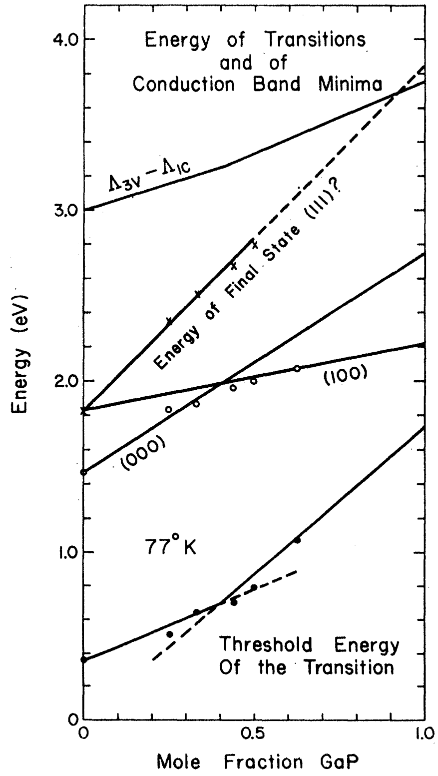

FIG. 11. Energy of transitions and of conduction-band minima of $Ga(As_{1-x}P_x)$ as a function of mole fraction GaP.

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[34] J. Callaway, J. Electron. **2**, 330 (1957).
[35] E. Haga and H. Kimura, J. Phys. Soc. Japan **19**, 1596 (1964).

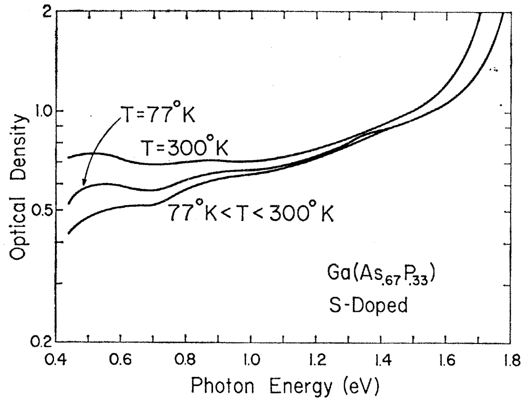

FIG. 12. Optical density of a S-doped Ga($As_{0.67}P_{0.33}$) sample as a function of photon energy at several temperatures.

plotted in the lower part of the figure. In the upper portion are plotted the approximate values of the (0,0,0) and (1,0,0) band gaps. The open circles represent the energies at which the band-gap absorption constant is 150 cm^{-1} for the samples measured, and is an indication of the Fermi level since transitions from the valence to conduction band must end at an empty state. At the top of the figure are plotted the energy of the $\Lambda_{3v} \rightarrow \Lambda_{1c}$ transitions[22] at 80°K and the energy of the final state, which is obtained by adding the threshold energy and the estimated energy of the Fermi level as given by the open circles. We see that the energy of the transition is larger than the separation of the (0,0,0) and (1,0,0) minima. The energy of the final state is near the energy of the (1,0,0) minima only for $x=0.0$.

The point at $x=0.625$ may be in error. As seen in Fig. 7 only a slight nonlinearity is observed for sample 15. This is further seen in Fig. 10. At this wavelength, a mistake of judging the threshold by only 500 Å changes the energy of the threshold by 0.05 eV. Furthermore, it is not known whether the initial state is the (1,0,0) minima or the associated indirect-donor level. This could change the energy of the final state by as much as 0.1 eV. It is clear that the extrapolation to GaP shown by the dashed line is not valid if the explanation given below is correct. It would seem that the curve must bend down for large values of x, or the curve, if linear, must have a lower slope.

The final state may be the (1,1,1) minima, or another point in the Brillouin zone which satisfies the relation[36]

$$\mathrm{grad}_k E_{\mathrm{initial}}(k) = \mathrm{grad}_k E_{\mathrm{final}}(k). \tag{5}$$

Thus, the maxima between the (0,0,0) and (1,0,0) or (1,1,1) minima, or a saddle point, could be a final state. However, the lifetime for a maximum would probably be so small that it would amount to a virtual state, and the electrons would fall to lower minima.

Various authors have reported the energy of the $\Lambda_{3v} \rightarrow \Lambda_{1c}$ transitions in Ga(AsP).[22,23,37] Thompson *et al.*[37] have explained their spin-orbit splitting data as being due to a shift in position of the Λ transitions in k space from a point with large k toward $k=0$. The energy of the Λ transitions in GaAs is of nearly the same energy as the $L_{3v} \rightarrow L_{1c}$ transitions, and the energy of the (1,1,1) minima is only slightly less than the energy of the final states of the $\Lambda_{3v} \rightarrow \Lambda_{1c}$ transitions. Thus for GaAs the difference in energy of the Λ transitions subtracted from the energy of the (1,1,1) minima is roughly the energy of the valence band at the point in k space where the Λ transitions take place. This is not so for Ga(AsP), because as the point in k space where Λ transitions take place shifts toward Γ with larger x, the final state at Λ_{1c} is at a higher energy than the (1,1,1) minimum. Thus, the energy of the (1,1,1) minimum should always be less than the energy of the Λ transition, and the extrapolation and the point at $x=0.625$ as shown in the (1,1,1) energy curve in Fig. 11 may not be valid. Furthermore, in order to be consistent with the spin-orbit splitting data of Thompson *et al.*, the curve for the (1,1,1) minima should probably have less slope than shown for $x<0.4$ or 0.5 (this is possible if the $x=0.0$ point is too low), and then turn upward near $x=0.4$ or 0.5. The alternative to this explanation is that the energy of the valence band at L is much greater for GaP than for GaAs, and this is highly unlikely.

Thus the proposition that the final state for the transitions reported here is the (1,1,1) minima is not inconsistent with reflectivity data, within the limits of possible large experimental error for these measurements. The extrapolated data for GaP disagree with the speculation of Subashiev and Chalikyan[38] based on a study of the fundamental absorption edge, and it is at variance with the GaP zone structure obtained by pseudopotential calculations.[22] The method used in this report is, however, more reliable, and gives a better estimate of the position of the (1,1,1) minima in GaAs, Ga(AsP), and GaP.

Curve fitting of the excess absorption using the equations of Haga and Kimura[35] has been attempted here, but the best fit showed that the effective mass of the final state is less than the effective mass of the (0,0,0) minimum, a fact that present pseudopotential calculations contradict. This also does not seem possible considering the discussion above of the Λ transition. A further pertinent result is that the virtual state for the transition is in the (1,1,1) conduction band or the (0,0,0) minimum, and not in a higher-lying minimum.

Figure 12 shows the optical density of a sulfur-doped Ga($As_{0.67}P_{0.33}$) sample in the interconduction-band transition region. The optical density is proportional approximately to the absorption constant. The absorption constant was not calculated for this sample, as there were voids in the crystal and a pinhole allowed

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[36] J. C. Phillips, Phys. Rev. **104**, 1263 (1956).

[37] A. G. Thompson, M. Cardona, K. L. Shaklee, and J. C. Woolley, Phys. Rev. **146**, 601 (1966).

[38] V. K. Subashiev and G. A. Chalikyan, Phys. Status Solidi **13**, K91 (1966).

light to shine directly through the sample. The intermediate temperature measurements were made as the Dewar was warming, and the temperature for this curve is not constant. The essential features, however, are shown. The slight peak at 0.85 eV is probably due to an unidentified impurity.

The effects of the indirect donor level on the electrical properties of this sample were previously reported.[28] The explanation for the change in absorption constant follows closely the explanation for the change in electrical properties. At 77°K the indirect donor level is near the Fermi level for sulfur-doped $Ga(As_{0.67}P_{0.33})$ inasmuch as sulfur has a high ionization energy. The (0,0,0) minimum is somewhat depopulated by the indirect donor level, and in contrast with the Te- and Se-doped samples described above, the absorption constant is smaller than for 300°K. As temperature is increased, the indirect conduction band and donor levels shift down relative to the (0,0,0) minimum, further depopulating the (0,0,0) minimum and lowering the absorption constant. Further increase of the temperature causes the indirect minima and associated indirect donor levels to drop still more, but the Fermi function spreads, depopulating the indirect donor level, increasing the number of electrons in the (0,0,0) minimum, and causing the absorption constant to rise. Recent resistivity measurements by G. E. Stillman of this laboratory confirm this previously postulated population of the (0,0,0) minimum with temperature. Thus, absorption measurements provide a method to study the effects of the indirect donor level and confirm earlier observations.[28]

Fundamental Absorption Edge

Most of the samples studied here are heavily doped and show some of the effects expected for impure semiconductors. As seen in Figs. 4 through 7, the absorption edge in heavily doped Ga(AsP) has an exponential dependence on photon energy. As explained for GaAs by Lucovsky,[39] this is due to transitions between acceptor and donor bands which have a Gaussian shape. There are no acceptor levels intentionally added to these samples, but impurities can find their way into the crystals, e.g., Si which is amphoteric and can act as a donor or acceptor, as previously discussed.

Shifts in the measured band-gap energy of Ga(AsP) due to doping are very evident. Figures 4 through 7 show the spread of energy for various values of composition x. We see that the curve of sample 8 with $x=0.3$ and 3.9×10^{18} carriers per cm^3 is shifted into the curves for $x=0.33$ for crystals of less doping. Figure 13 shows at 300 and 77°K the energy at which $\alpha=100$ cm^{-1} for several samples of composition $x=0.25$, 0.30, and 0.33 as a function of carrier concentration. In these cases it is obvious that the band gap is larger for higher doping, consistent with the Burstein shift. One $x=0.33$ point at 300°K falls far off the plotted curve, and from Table III we see that this sample (number 9) is nondegenerate. The nondegeneracy may be due to partial compensation, which would lower the energy gap. From Fig. 13 we see that the energy changes with temperature by about the same amount for each value of x, but there is more than the expected variation from $x=0.25$ to $x=0.30$ at both temperatures. The variation from $x=0.30$ to $x=0.33$ is about correct. One point for $x=0.25$ is near the expected value. The two $x=0.25$ points, which are low, are for Se-doped crystals. The point near the correct value is for a Te-doped crystal. Thus there may be some effect on the optical band gap due to the dopant. No calculations for the Burstein shift using the equation of Kaiser and Fan[40] was performed since α_0, the absorption constant for pure material, was not known, and the samples described here are doubtless compensated.

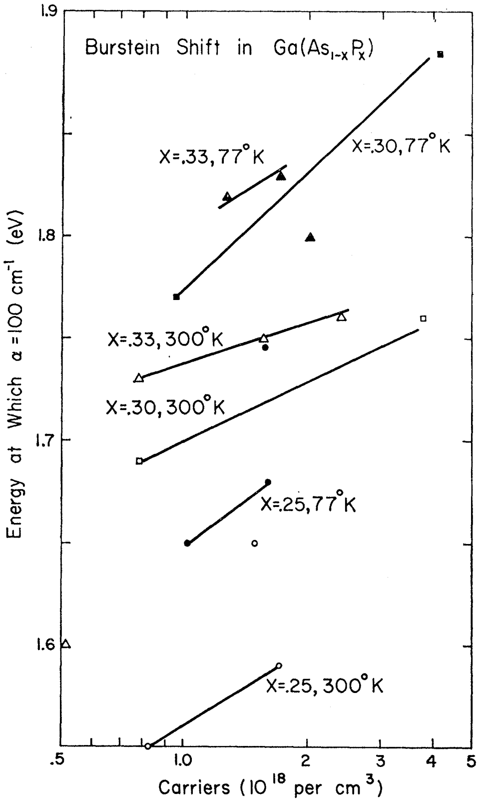

FIG. 13. Energy at which $Ga(As_{1-x}P_x)$ absorption constant is 100 cm^{-1} at 300 and 77°K as a function of carrier concentration with mole fraction GaP a parameter.

Shifts of absorption to lower values of energy are even more obvious than shifts to higher energy. Sample 2 with $x=0.125$ was grown with a large quantity of Te in the ampule and should have been strongly n-type. This is, however, material with a measured resistivity of 10 Ω cm and a room-temperature carrier concentration of only 1.76×10^{16} carriers per cm^3, indicating

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[39] G. Lucovsky, Solid State Commun. 3, 105 (1965).

[40] W. Kaiser and H. Y. Fan, Phys. Rev. 98, 966 (1955).

strong compensation. The low mobility indicates a large impurity concentration, and the low free-carrier absorption is another indication of compensation. The effect on the band gap is evident in Figs. 4 and 6. The band-gap energy shifts to lower values, lower, in fact, than the band-gap energy for pure GaAs. The total shift appears to be about 0.15 eV, and is due to transitions from a filled acceptor level to an empty donor level which overlaps the conduction band.[39]

The exponential slope defined by the constant m when the absorption constant is written as $\alpha \propto e^{mE}$ is given in Table III. The results of Lucovsky's theory are that the slope is less in more compensated materials and does not change much with temperature.[39] This is seen also for sample 2. There are other samples (10,15) whose slopes do not change much with temperature, but are about average for their value of mole fraction GaP. These samples do not appear compensated. The slope of the absorption edge seems to decrease for larger values of x, although the crystals are not more compensated. The cause for this is unknown at this time, but it is possible that when the (1,0,0) minima are sufficiently close to the Fermi level [which is above the (0,0,0) minimum in heavily doped GaAs-rich material], then indirect transitions may be as favorable as direct transitions to a state near the Fermi level. It may also be due to the fact that absorption is higher for alloys with composition x near 0.5, and the slope is calculated for a comparatively low value of absorption constant where the curved portion or "tail" of the absorption curve interferes in high-absorption material.

The "tail" at the absorption edge in the samples described here appears to be due to the addition of free-carrier absorption and band-to-band transitions to the fundamental edge absorption, rather than due to disorder effects. Subtracting the free-carrier and band-to-band absorption from the measured curve gives almost a straight line on a semilog plot. There is difficulty in doing this accurately since the slope of the band-to-band absorption curve at energies higher than band gap is not well known. Samples with very heavy doping (e.g., sample 8) do show a much more pronounced rounding near the absorption edge. This appears to be due to optically active un-ionized n-type dopants as proposed by Vieland and Kudman,[33] and is the reason that the band-to-band transition discussed above is difficult to see in heavily doped material (see Fig. 4). In the curves for sample 7 at 300°K, and samples 4 and 7 at 77°K, we see a change in slope at 1.1 eV that is probably due to transitions from acceptor states.[41] The acceptor states appear to be about 0.5 eV above the valence band and are most likely due to deep-level contaminating impurities.

Finally, we mention that the results we have presented are to some extent affected by crystal purity. In contrast to earlier work, however, these results are for well-annealed, homogeneous crystals which uniformly yield lasers of predictable wavelength.[16] Hence, this study is believed to be truly representative of $\mathrm{Ga(As_{1-x}P_x)}$ and its band structure (adjustable).

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[41] W. J. Turner and W. E. Reese, J. Appl. Phys. **35**, 350 (1964).