These results indicate that the 300°K fluorescence for p-type GaAs does not involve the acceptor states. The fluorescence for lightly doped n- and p-type GaAs occurs at nearly the same energy as the energy gap. However, for heavily doped n-type GaAs, the recombination leading to the fluorescence seems to originate at an energy 1 to 2 kT below the Fermi level as computed from the absorption measurements.

IV. SUMMARY AND CONCLUSIONS

From the absorption measurements it can be seen that in general the shifts of the absorption edge with increased doping level occur in either direction and can be divided into two components. The shifts to higher energy predominate in n-type GaAs at 77°K and the shifts to lower energy predominate in p-type GaAs at 300°K. The shifts to higher energy are caused by the change of the Fermi level with doping. The shifts to lower energy can probably be explained as an effective decrease in the band gap. An additional phenomena which should be taken into account is the change in energy gap which occurs when the lattice parameter changes with doping level. The Burstein type shifts are not satisfactorily explained in detail by Eq. (1). This is not too surprising for such a simple theory, but it is of interest to know where the principal

difficulties lie. Part, but not all of the problem lies in not accounting for the nonparabolic nature of the conduction band. The effect of impurities in decreasing the band gap mentioned in the previous paragraph if understood and properly accounted for may explain most of the remaining differences. The shifts observed for heavily sulfur-doped GaAs are anamolous and not understood at the present time.

From the fluorescence measurements we see that the acceptor state is involved in the recombination which leads to fluorescence at 77°K, but not at 300°K. In addition we have seen that Ge as a dopant in GaAs produces a deep level, presumably an acceptor state roughly 0.08 eV above the valence band edge. The n-type fluorescence occurs essentially at the band gap energy for low doping levels and although the fluorescence energy increases at the highest doping levels, the recombination resulting in this emission does not primarily involve carriers in the neighborhood of the Fermi level.

Conduction Band Minima of Ga(As$_{1-x}$P$_x$)†

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Photoresponse of surface barriers on samples of Ga(As$_{1-x}$P$_x$) covering the range $0 \leq x \leq 1$ has been measured. Thresholds corresponding to both direct and indirect band-to-band excitations within the semiconductor and also photoinjection from the metal have been identified. The threshold of the direct transition varies with composition from 1.37 eV in GaAs to 2.65 eV in GaP. The indirect transition was followed for $x \gtrsim 0.38$ and again varied linearly from 2.2 eV in GaP to an extrapolated value in 1.62 eV in GaAs. The energy separation of the two conduction band minima in GaAs is in disagreement with previously reported values.

I. INTRODUCTION

IT has been demonstrated in recent work, that when the photovoltaic response is measured for a Schottky barrier at a clean metal-semiconductor interface, the response has two distinct spectral regions. The first region is where the photon energy exceeds E_g the energy gap of the semiconductor, and electron transitions take place from the valence to the conduction band. The second region, where $h\nu < E_g$ is generally a region where

the response per photon is much smaller, and a number of recent studies[1-9] have attributed this response to

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photoemission of electrons (or holes) from the metal over the Schottky barrier. The present work consists of the application of this experimental method to the Ga(As$_{1-x}$P$_x$) system. The photoresponse has been measured on samples covering the range from $x=0$ to $x=1$. Of particular interest is the range where $h\nu > E_g$. For $x>0.38$, the response is resolved into two distinct regions, one due to indirect or phonon aided transitions and the second due to direct transitions. The threshold of the direct process could be followed across the entire composition range and the indirect process from $x\approx 0.38$ to $x=1.0$.

II. BACKGROUND

Considerable effort has been devoted to the study of the structure of the conduction band in elemental and compound semiconductors. Of particular interest in the present study, is the work which has attempted to identify the relative positions of the (000) and (100) minima in GaAs and GaP.

Ehrenreich[10,11] and Paul[12] have reviewed most of the experimental evidence for the position of these minima. Ehrenreich concludes that the (100) minima are 0.36 eV above the $\mathbf{k}=0$ minimum in GaAs while in GaP the two minima reverse positions with an energy separation of about 0.35 eV. In each case the deeper of the two minima forms the bottom of the conduction band.

That the conduction band minimum is not at $\mathbf{k}=0$ in GaP can be concluded from the spectral shape of the absorption edge[13] and the large value of the electron effective mass.[14] The pressure dependence of E_g and resistivity suggest (100) minima.[11,12,15] Experimental evidence for the higher $\mathbf{k}=0$ minimum comes from optical measurements where the interpretation has been shown to be questionable. Absorption edge measurements indicate the beginning of a rapidly rising absorption starting approximately 0.35 eV above the indirect threshold.[13] However, Paul[12] points out that the pressure dependence of the absorption edge leads to a separation of ~ 1 eV for the two minima if a specific functional form is assumed for the pressure dependence of the indirect transition. An infrared absorption band observed in n-type GaP had been tentatively assigned[13] to interband transitions between the two minima. However, later work[12] showed that the absorption band position had a much smaller pressure dependence than was expected from the pressure coefficient of the two minima. It has also been suggested[16] that the band is due to a 0.4 deep oxygen impurity level.

The primary evidence for the energy separation of the two minima in GaAs comes from the analysis of the temperature dependence of the Hall coefficient.[10,17] There is considerable evidence that the $\mathbf{k}=0$ minimum is the bottom of the conduction band; however, the exact value of E_g appears to be in question. Numerous absorption edge measurements[18-21] show the room temperature absorption to start at 1.37 ± 0.02 eV. However, theoretical fits to the data[18,22] in the high absorption regions give values for E_g of 1.41 eV and 1.43 eV. The absorption curves of one of these studies[22] also shows evidence for direct exciton formation. Recent measurements[23] of electroluminescent band-to-band recombination radiation in shallow p-n junctions show peaks near 1.36 eV and 1.39 eV. The authors interpret these emission bands as the indirect and direct transitions, respectively, where the indirect transition arises from the splitting of the heavy hole band degeneracy via spin-orbit interaction. There has been recent evidence[21] that E_g is impurity concentration-dependent. There is also an infrared absorption band[20] in n-type GaAs which had been interpreted in terms of interband transitions, but in view of the GaP results, this interpretation must be regarded as suspect. It has been indicated[12] that there is some difficulty with the interpretation of the pressure dependence of the GaAs resistivity when the 0.36-eV separation is assumed.

Much of the justification for Ehrenreich's analysis[11] comes from absorption edge data on Ga(As$_{1-x}$P$_x$) solid solutions. These measurements indicate an abrupt change in the variation of the intrinsic absorption edge with composition near $x=0.5$. Linear extrapolations of the two portions of the curve gave energy separations in the cases $x=0$ and $x=1$ which were in general agreement with the above quoted values. However, examination of the results show that the scatter in the experimental data and the necessity of extrapolating over a 50% composition range introduces a substantial uncertainty (tenths of an eV) into the position of the higher lying minimum in each case.

III. EXPERIMENTAL

Samples were prepared on material obtained from several industrial laboratories. Surface received various chemical treatments depending upon condition but were always cleaned in HF for at least 15 min prior to placing in an oil-free vacuum system. Gold films up to ~ 1000 Å thick were deposited on the surface by evap-

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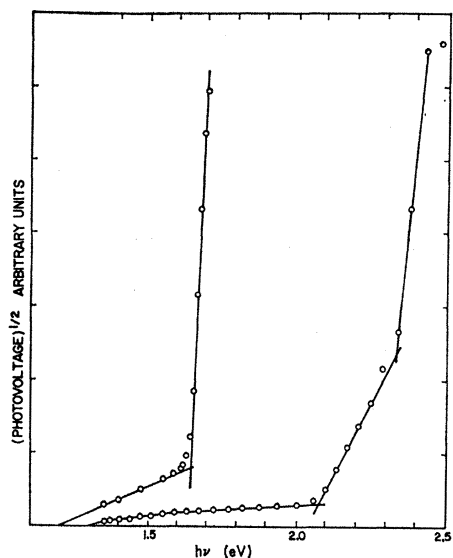
FIG. 1. The room-temperature (photovoltage)$^{1/2}$ versus photon energy for two samples of Ga(As$_{1-x}$P$_x$). Where the data points are for $h\nu \lesssim 1.7$ eV, the sample has $x=0.20$. The other sample has $x=0.78$.

oration in the form of 0.01 in. diam. dots at a residual were gas pressure of $<10^{-6}$ Torr. The photoresponse data taken using a quartz prism monochromator equipped with a 50-cps shopping system and synchronous detection. The units were illuminated from the metal side (front wall configuration). Several samples were made with aluminum dots in addition to the gold, and in these cases the results were essentially identical. The form of the response for $h\nu > E_g$ was found to be independent of the thickness of the metal layer.

In most cases the composition values were obtained from x-ray fluorescence measurements by comparison of the As K_α and Ga K_β lines which occur at close to the same energy. The estimated over-all accuracy in the composition determined by this method is $\pm 2\%$. In the few cases for which fluorescence measurements were not made, the composition was supplied by the laboratory in which the sample was grown. These values were determined by lattice constant measurements.

Neglecting phonon energies the absorption coefficient, α, for indirect transitions is given by

$$\alpha = (C/h\nu)(h\nu - h\nu_i)^n,$$

where $h\nu_i$ is the threshold energy and n is close to 2.0. A value of $n=2.2$ has been reported[13] for GaP. If the optical attenuation length $1/\alpha$ is large compared to the minority carrier diffusion length L, and the width of the depletion layer, then the number of electrons per incident photon is proportional to α. If $h\nu$ is close to $h\nu_i$ then the photoresponse will be proportional to $(h\nu - h\nu_i)^2$. Therefore, under these assumptions, a (photovoltage)$^{1/2}$ versus $h\nu$ plot may be expected to show a linear region where indirect transitions are dominant. Photoresponse

curves for two samples of widely different compositions are shown in Fig. 1. The left curve shows emission from the metal into the semiconductor followed at higher photon energy by an abrupt increase in response due to semiconductor band-to-band excitation. The second curve shows low energy response from the metal followed by two well-resolved intrinsic excitation processes within the semiconductor. The lower of these follows a second power dependence as expected for an indirect transition. The increase in response due to the higher transition is sufficiently rapid that its functional form is difficult to determine and, as will be shown, is ascribed to a direct transition. The fact that changes in α up to a level of 10^4 cm^{-1} are observed in the photoresponse indicates a very short L which is consistent with the small minority carrier lifetimes in these materials.[24]

The photothresholds for each region were taken from the zero response after subtracting out the extrapolation of the response due to the lower energy processes. The error in the photothresholds is largely due to this extrapolation procedure and is estimated to be at most ± 0.02 eV. The measurements themselves were taken with a resolution of better than 0.01 eV.

For samples in which $x > 0.38$, the indirect transition occurs at lower energy than the direct and the position of both minima could be followed across the entire composition range to $x=1$. When $x<0.38$, the direct transition occurs at the lower energy and only the $k=0$ minimum could be followed. The results of these measurements are shown in detail in Fig. 2. The photothresholds measured by this technique on the terminal compounds are in good agreement with those obtained from optical absorption data.

In the present case the photovoltaic technique has advantages over optical absorption measurements. The direct edge can be seen on top of the indirect edge without the necessity of preparing micron thick-samples.
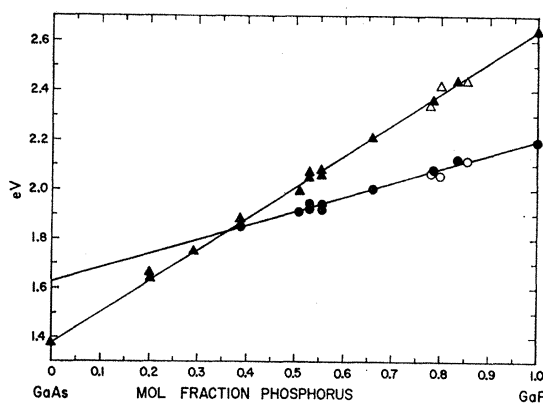

FIG. 2. A plot of the threshold energies as a function of the mole fraction of phosphorus. The dark points indicate samples where the composition was measured by x-ray fluorescence. Triangles correspond to the direct transition and circles to the indirect.

[24] C. Hilsum and A. C. Rose-Innes. *Semiconducting III—V Compound* (Pergamon Press, Inc., New York, 1961), p. 182.

Also the composition of the Ga($As_{1-x}P_x$) often varies through the thickness of the sample making direct absorption measurements unreliable. Many of the samples were only very thin epitaxial layers on GaAs, and could not have been used for studying the lower absorption coefficient regions.

IV. DISCUSSION OF RESULTS

In view of the results given in Fig. 2 the linear extrapolation procedure used by Ehrenreich is well justified. There is no question that the rapid rise in the absorption edge of GaP near 2.65 eV is due to the same type of optical transitions which are responsible for the absorption edge in GaAs; direct transitions to the conduction band minimum at $k=0$. It may be noted that the energy separations for the two minima for $x=0$ and $x=1$ are are not the same as those previously reported.[11] For GaP it was pointed out that the value of this separation (~ 0.35 eV) as well as the identification of the minima involved was not on a very sound basis. The value from Fig. 2 is 0.45 ± 0.04 eV. It should be pointed out, however, that this value is the difference in photothresholds. Assuming previously reported phonon energies for the indirect transition[25] the energy separation could be as low as 0.40 ± 0.04 eV assuming no contribution to the photoresponse from direct exciton formation.[22,26] In GaAs the separation of the thresholds is smaller since the crossover is at $x \approx 0.38$ rather than at $x \approx 0.55$ as previously reported. The higher threshold was obtained by extrapolation but should be accurate within ± 0.03 eV. Accounting for the maximum GaAs phonon energy[27,28] the separation of the minima could be as large as 0.28 ± 0.05 eV. This result is in disagreement with the 0.36-eV value deduced from Hall data. It should be noted that it is assumed that the response near the 1.37-eV threshold, which is a region of low-absorption coefficient, arises from direct transitions to the $k=0$ minimum. If the E_g values deduced from the high-absorption region[20,24] are used, then the energy separation would be reduced by 0.04 to 0.06 eV. Care was exercised to use nondegenerate samples to eliminate band filling[29] effects.

Careful photomeasurements were made on GaAs in the 1.5- to 1.8-eV region in an attempt to observe structure due to the presence of the indirect transitions. A small increase was noted near 1.7 eV. If one assumes the indirect transitions follow the same spectral form as in GaP and that the increase corresponds to an additional absorption coefficient of ~ 100 cm^{-1} according to $\Delta R/R \approx \Delta \alpha / \alpha$, where $R =$ response, then the indirect threshold would be near 1.6 eV in rough agreement with 1.62-eV value of Fig. 2. However, the spin-orbit splitting of the valence band[30,31] is 0.33 eV and the structure could also be due to direct transitions from the split off band. The absorption threshold here would be 1.68 eV. No evidence was seen for the spin-orbit splitting of the degenerate heavy-hole band[23]; however, this would appear as only a slight rounding at the bottom of the direct edge and would be difficult to separate from the metal photoresponse.

Note added in proof. After the completion of this work, there appeared a note by N. Holonyak, S. F. Bevacqua, C. V. Bielan, and S. J. Lubowski, Appl. Phys. Letters **3**, 47 (1963), in which emission from laser diodes of Ga(As-P) was studied. The conclusions drawn concerning the onset of the indirect transition are a striking confirmation of our results. Also, a very recent study of optical absorption in n-type GA($As_{1-x}P_x$) in the 3μ region has been reported by J. W. Allen and J. W. Hodby, Proc. Phys. Soc. (London) **82**, 315 (1963). They conclude that below room temperature the 3μ the GAP absorption band is associated with vertical transitions from hydrogen-like donor states near the conduction band minimum to a higher conduction band. Above room temperature transitions from the lowest conduction band must also be considered. These results tend to confirm a proposal previously made by W. Paul[12] for the origin of this band. The authors wish to thank R. Zallen for bringing this later work to their attention.

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