

(A).<sup>16,17</sup> In both GaP:Bi and GaP:N this leads to a ratio of vibronic to no-phonon components that is much greater for the *B* spectrum. The absence of comparable ratio changes in our *L*, *M*, and *H* spectra indicates that the oscillator strength scheme is not satisfactory, and it leaves us with the Jahn-Teller effect as the most probable explanation of the unusual temperature dependence.

*Note added in proof.* A true Jahn-Teller effect requires the degeneracy of the electronic wave function. In the present case we have no indepen-

dent evidence of such degeneracy. In the absence of degeneracy a low-temperature lattice distortion may occur nevertheless, and it is sometimes called a pseudo-Jahn-Teller effect.

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## Photoluminescence Processes in $\text{In}_{1-x}\text{Ga}_x\text{P}$ at 2°K

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Photoluminescence measurements on  $\text{In}_{1-x}\text{Ga}_x\text{P}$  have verified the location of the direct-indirect conduction-band crossover at  $x=0.74$ ,  $E_g=2.33$  eV at 2°K. The photoluminescence spectra observed are InP-like for  $x<0.68$  and GaP-like for  $x>0.72$ . Shallow bound excitons are observed with indirect gap  $\text{In}_{1-x}\text{Ga}_x\text{P}$ . Curvature in the relationship between the bound exciton energy and alloy composition suggests curvature of the indirect  $\Gamma_{8v}$ - $X_{1c}$  band gap as a function of alloy composition (maximum deviation from the linear dependence is estimated at 22 meV). Shallow donor states seem to be tied rigidly to their conduction bands. No mixing of the  $\Gamma$  and  $X$  conduction-band donor ground states has been observed. Thus, significant mixing occurs over a range less than  $\Delta x=0.02$ , the compositional resolution in the present measurements.

### I. INTRODUCTION

We present here the results of a study of the photoluminescence (PL) of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  at 2°K. The results give an understanding of the luminescence processes that occur in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  and other III-V

alloys in general, especially with respect to the changes in luminescence mechanisms that occur concurrently with the crossover between the direct and indirect conduction bands. At the same time this study has furnished precise data on the behavior of impurity states in the alloy. Low-tem-

perature PL measurements, when sharp-line spectra are observed, prove to be an excellent method for monitoring the alloy-composition dependence of the indirect band gap.

Previous studies of luminescence processes in alloys include a study of the electroluminescence in the conduction-band crossover region of  $\text{GaAs}_{1-x}\text{P}_x$  by Herzog *et al.*,<sup>1</sup> and of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  by Onton and Lorenz.<sup>2</sup> Merz and Lynch<sup>3</sup> have observed donor-acceptor pair emission in indirect-band-gap  $\text{Ga}_{1-x}\text{Al}_x\text{P}$ , and Williams *et al.*<sup>4</sup> described evidence for donor-acceptor pair emission in the indirect-band-gap range of  $\text{In}_{1-x}\text{Ga}_x\text{P}$ . Kressel *et al.*<sup>5</sup> have studied cathodoluminescence of indirect-band-gap  $\text{Ga}_{1-x}\text{Al}_x\text{As}$ . Recently Chevallier and Rodot<sup>6</sup> reported bound-exciton recombination in indirect-band-gap  $\text{In}_{1-x}\text{Ga}_x\text{P}$ . With the exceptions of the studies by Herzog *et al.*<sup>1</sup> and Kressel *et al.*,<sup>5</sup> however, these investigations involved luminescence through relatively deep unknown impurity centers, or else lacked sufficient systematic data to lead to definitive conclusions about the alloy-composition dependence of the band gap or the nature of bound states in the alloy. The results on those features obtained by Herzog *et al.*<sup>1</sup> with  $\text{GaAs}_{1-x}\text{P}_x$  and those presented here for  $\text{In}_{1-x}\text{Ga}_x\text{P}$  mutually support each other.

## II. EXPERIMENTAL

### A. Materials Preparation

The  $\text{In}_{1-x}\text{Ga}_x\text{P}$  crystals used in these experiments were grown either by a modified Bridgman two-zone synthesis<sup>7</sup> or by a solid-liquid-solid technique.<sup>8</sup> Crystals grown by the Bridgman technique had both longitudinal and radial composition gradients varying between GaP and InP. With the solid-liquid-solid technique the composition of the ternary alloy was much more homogeneous. Selected wafers could be found that had essentially no composition gradients over dimensions as large as  $0.25\text{ cm}^2$ .

The Te doping was accomplished by adding the dopant directly to the charge. The resulting crystals were *n*-type and Hall measurements were made on representative samples. Spiders were cut from crystals grown by the solid-liquid-solid technique and van der Pauw specimens were cut from the Bridgman grown crystals. The measured carrier concentrations were in the  $10^{17}$  carriers/ $\text{cm}^3$  range, indicating that the conduction processes were dominated by the Te dopant. In general, the net Te concentration as determined by electrical measurements seemed to increase with the In content of the alloy.

### B. Optical Measurements

For the PL measurements irregularly shaped

samples with linear dimensions in the range 0.1–0.3 mm were used. If a sample did not have a large cleaved flat face, one was prepared by lapping and polishing. The alloy composition of these samples was measured at several points on the flat face by electron microprobe. The accuracy of this composition measurement is estimated at  $\Delta x = \pm 0.025$  for  $x$  in  $\text{In}_{1-x}\text{Ga}_x\text{P}$ . The precision in  $x$  is better, approximately  $\pm 0.015$ . A more detailed description of electron-probe microanalysis of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  has been given by Onton *et al.*<sup>9</sup>

The PL was measured with samples cooled to about  $2^\circ\text{K}$  by immersion in pumped liquid helium. The luminescence was excited with the  $4880\text{-}\text{\AA}$  emission of an argon-ion laser. The PL was analyzed with a Perkin-Elmer 98G monochromator, employing a 1200-line/mm grating and slit widths in the 50- to  $100\text{-}\mu\text{m}$  range. Photomultipliers with S-1 and S-20 spectral responses were used as detectors. The spectra shown have not been corrected for wavelength variations in spectrometer response.

## III. PHOTOLUMINESCENCE RESULTS

PL spectra representative of those observed in all alloy composition ranges are shown in Fig. 1. Each of the spectra is normalized to the same

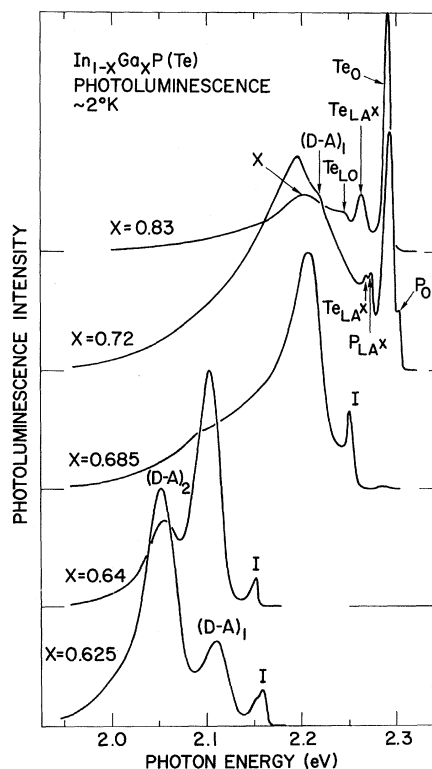


FIG. 1. PL spectra of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  for five alloy compositions. The spectra have been displaced relative to each other for graphic clarity.

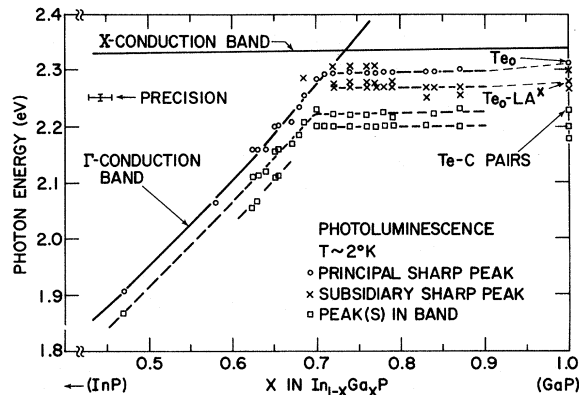


FIG. 2. The energies of the conduction-band minima of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  relative to the top of the valence band and energies of PL spectral features as a function of alloy composition in the range  $0.45 < x < 1.00$ . For GaP the energy of the exciton bound to neutral Te donors and three of its phonon replicas are shown, as well as the location of the peak of the Te-C pair band and its local and lattice mode replicas.

maximum intensity, and the curves have been displaced relative to each other vertically for clarity. Correction of these spectra for S-20 photomultiplier response would not affect the appearance of the spectra significantly.

The spectral peak positions in these spectra and additional spectra not shown in Fig. 1 are plotted as a function of the alloy composition parameter  $x$  in Fig. 2 for  $0.45 < x < 1.0$ . Also shown in Fig. 2 by the solid lines are the energies of the  $\Gamma$  and  $X$  conduction-band minima relative to the top of the valence band. The alloy composition dependence of the  $\Gamma$  conduction-band minimum at  $2^\circ\text{K}$ ,  $E_{\Gamma}^{2^\circ\text{K}}(x)$ , is given by

$$E_{\Gamma}^{2^\circ\text{K}} = 1.409 + 0.695x + 0.758x^2 \text{ eV}, \quad (1)$$

where  $x$  is the alloy composition parameter. Equation (1) has been obtained by adjusting the  $300^\circ\text{K}$   $\Gamma$  energy gap of  $\text{In}_{1-x}\text{Ga}_x\text{P}$ <sup>9,10</sup> for the lower temperature used here. The temperature dependence of the  $\Gamma$  energy gap of  $\text{In}_{1-x}\text{Ga}_x\text{P}$  has been estimated by a linear interpolation between the measured temperature dependencies of InP<sup>11</sup> and GaP.<sup>12</sup> The alloy composition dependence of the indirect  $\Gamma_{8v} \rightarrow X_{1c}$  energy gap has been assumed to be linear in  $x$ , with a value of 2.32 eV in InP<sup>13,14</sup> and 2.338 eV in GaP.<sup>15</sup> The direct-indirect conduction-band crossover thus occurs at  $x = 0.74$  with  $E_g = 2.33$  eV at  $2^\circ\text{K}$ .

The PL spectra are characteristic of direct-band-gap processes for  $x < 0.68$ . Spectra with features characteristic of both direct and indirect recombination are observed for  $0.68 < x < 0.72$ , and spectra characteristic of indirect-band-gap

recombination for  $x \geq 0.72$ .

#### IV. DISCUSSION

##### A. General Features

PL spectra typical of direct-band-gap recombination are shown for  $x = 0.625$  and  $0.64$  in Fig. 1. There are three principal peaks in these spectra. Intrinsic recombination is denoted by I. Within I we include the possibility of very shallow ( $\leq 5$  meV) bound exciton and free-hole bound-donor-electron recombination since the experimentally observed nonresolution-limited linewidth of I is of the order of  $\geq 7$  meV. However, substructure in I, unless reproduced in several samples, is suspect since the same effect could be produced by alloy composition gradients of the order of  $\Delta x = 0.005$ . We recognize that the apparent substructure in I for  $x = 0.625$  in Fig. 1, for example, is consistent with substructure observed in the near-band-gap PL of InP.<sup>11,16</sup> However, the more likely explanation at this time is that these observed features arise from slight alloy composition variations, and that I is an unresolved combination of near-band-gap recombination processes that have been identified in InP<sup>16</sup> [free exciton, bound exciton, (free-hole)-(shallow bound-donor-electron) recombinations]. The next two spectral peaks, occurring at lower energies than I and denoted by  $(D-A)_1$  and  $(D-A)_2$ , result from donor-acceptor pair recombination. Typically the peaks of  $(D-A)_1$  and  $(D-A)_2$  occur, respectively, 45–50 meV and 90–100 meV lower in energy than the peak of I for  $0.50 \lesssim x < 0.68$ . Various relative intensities of I,  $(D-A)_1$ , and  $(D-A)_2$  have been observed in different samples, varying from I dominant to  $(D-A)_2$  dominant. In some samples  $(D-A)_2$  was no more than a tail on  $(D-A)_1$ . This is evidence against the hypothesis that  $(D-A)_1$  and  $(D-A)_2$  are related by a lattice or local mode. The linewidths of  $(D-A)_1$  and  $(D-A)_2$  were typically in the range of 30–40 meV, indicating by comparison with InP<sup>17</sup> that the pair recombination under the conditions employed was nearly saturated. The intrinsic recombination peaks I, with  $x$  up to 0.70, lie within experimental uncertainty on the  $\Gamma$  conduction-band line in Fig. 2. Thus those data at  $2^\circ\text{K}$  and previous room-temperature measurements<sup>9,10</sup> are mutually consistent in their identification of intrinsic direct-band-gap recombination.

A typical PL spectrum from the GaP-rich end of the  $\text{In}_{1-x}\text{Ga}_x\text{P}$  alloy system is represented by the spectrum for  $x = 0.83$  in Fig. 1. It is dominated by a relatively sharp (half-width = 9 meV) line  $\text{Te}_0$  which we ascribe to the recombination of an exciton bound to a neutral Te donor (in GaP the same exciton has a width of  $\lesssim 0.3$  meV at Te concentrations less than  $10^{17} \text{ cm}^{-3}$ ). At somewhat

lower energies two-phonon-assisted replicas of this exciton recombination are observed and then a band labeled  $X$ , which will be discussed later. There does not appear to be a significant difference in these phonon energies from those observed in GaP.<sup>18</sup> A PL spectrum similar to that for  $x=0.83$  is observed with  $x=0.72$  (see Fig. 1). Here, however, an additional bound-exciton recombination denoted by  $P_0$  (and its phonon replica  $P_{LA}x$ ) is observed, as well as the donor-acceptor pair band  $(D-A)_1$ . The chemical species of the impurity involved in the  $P_0$  transition is unknown. Most likely it originates from recombination of excitons bound to neutral Si donors or acceptors as in GaP.<sup>18,19</sup> At the composition  $x=0.685$ , the location of the pair band remains at approximately the same energy as for  $x>0.685$ . However, the higher-energy emission I is now more similar to those observed with  $x=0.625$  and  $x=0.64$  than to the bound recombination with  $x=0.72$  and  $x=0.83$ .

The relationships of the various spectra in Fig. 1 are quite evident in the plot of Fig. 2. The  $Te_0$  exciton line lies on a line that has been drawn parallel to the  $X$  conduction band. This line extrapolates to 2.300 eV in GaP (at  $x=1.0$ ), about 10 meV below the position of the  $Te_0$  line in GaP,<sup>18,20</sup> 2.3102 eV. The free-exciton energy in GaP is 2.3225 eV at 2°K,<sup>15</sup> about 15 meV below the energy gap. The maximum binding energy of the  $Te_0$  exciton in the  $0.72 < x < 0.87$  range of alloy composition is thus estimated as 23 meV (note also the discussion in Sec. IV B). Such a shallow exciton should reflect the alloy composition dependence of the  $X$  conduction band within a few meV, as there are no apparent discontinuities in the exciton binding energy in this alloy composition range. Thus, without any detailed understanding of the bound exciton state observed in the alloy, these PL results confirm the position of the  $X$  conduction in  $In_{1-x}Ga_xP$  for  $x>0.72$ , i.e.,

$$E_{gX}^{2^\circ K}(x) = 2.321 + 0.017x \text{ eV.} \quad (2)$$

For  $x<0.72$ , if we assume that the  $X$  conduction band continues linearly with alloy composition, the position of the  $X$  point in  $InP$ <sup>13,14</sup> is verified to within  $\pm 30$  meV by the present data.<sup>21</sup> The possibility of small deviations from Eq. (2) is discussed in Sec. IV B.

At  $x=0.713$  the line denoting the alloy composition dependence of the  $Te_0$  exciton intersects the  $\Gamma$  conduction-band line, and at lower values of  $x$  the principal sharp high-energy line follows the  $\Gamma$  conduction-band line. Thus the lifetime of the indirect bound exciton  $Te_0$  should be short for decay to a direct electron-hole pair or exciton, compared to recombination as soon as this decay becomes energetically favorable. With one sample at  $x=0.685$  (see Figs. 1 and 2) a weak high-energy

PL peak was observed that may be the result of  $Te_0$  recombination with an exciton energy greater than the direct band gap. The effect was experimentally reproducible. However, the possibility that this small emission peak resulted from a minor inclusion of somewhat higher  $x$  alloy cannot be excluded.

Pair bands are observed in the indirect-band-gap range as in the direct-band-gap range of alloy composition. Here, however, the maximum in the principal band (denoted by  $X$  for the spectrum with  $x=0.83$  in Fig. 1) occurs 135–140 meV below the band gap given by Eq. (2). Often structure could be resolved on the high-energy side of this band [cf. the shoulder denoted by  $(D-A)_1$  for the spectrum with  $x=0.72$  in Fig. 1]. Since C is expected to be the principal acceptor in our samples, this band probably results from recombination between donors and C acceptors. Since the material has been intentionally Te-donor doped, the strength of this band probably results primarily from Te-C pair emission. However, we expect non-negligible numbers of S and Si donors in our alloy. S-C and Si-C pair bands could contribute to structure observed on the pair band. Thus an identification of structure such as  $(D-A)_1$  cannot be made. Likewise, the significance of the energy at the pair-band peak is lost for precise evaluation of donor and acceptor binding energies. However, it is significant to note that within experimental uncertainty the pair band and structure on it follows the same alloy composition dependence as the band gap [Eq. (2)]. The transition of the pair band from an indirect pair band (i.e., a pair band that follows the indirect-conduction-band alloy composition dependence) to a direct one occurs abruptly within the resolution of the present data. Since the direct or indirect nature of the pair band involves only the nature of the donor, this then indicates that significant mixing of the  $A_1$  ground state of the Te donor electron associated with the  $\Gamma$  conduction band and the  $A_1$  ground state of the Te donor associated with the three  $X$  conduction-band minima occurs at most over a range of 0.02 in  $x$ , the compositional resolution in these measurements. Thus we find the simple result that donor levels are quite rigidly attached to conduction bands in this alloy system. Variations in "shallow" donor binding energies with alloy composition seem to be minor, and the crossover between direct and indirect donor levels is abrupt for practical purposes.

In view of the fact that about 40 meV<sup>22</sup> (valley-orbit splitting) of the 89.8-meV<sup>20</sup> binding energy of Te donors in GaP is derived from local effects, it is somewhat surprising that substantial variations in indirect conduction-band donor binding energies with alloy composition are not noticeable. Yet

experimentally, within the resolution offered by donor-acceptor pair bands in luminescence, this relative invariance is borne out by the present results as well as others in  $\text{In}_{1-x}\text{Ga}_x\text{P}$ ,<sup>4</sup>  $\text{GaAs}_{1-x}\text{P}_x$ ,<sup>1</sup> and  $\text{Ga}_{1-x}\text{Al}_x\text{P}$ .<sup>3</sup>

The present results on  $\text{In}_{1-x}\text{Ga}_x\text{P}$  have a close analog in the  $\text{GaAs}_{1-x}\text{P}_x$  system. The latter system has been studied by Herzog *et al.*<sup>1</sup> There is an obvious one-to-one correspondence between every major detail in their study at  $77^\circ\text{K}$  and the present one. Thus an elaboration is not necessary. The present study, however, allows an extension of the interpretation given by Herzog *et al.*<sup>1</sup> Together, these studies suggest that what has been found here can be considered a general behavior of ternary III-V alloys.

The present study and that of Herzog *et al.*<sup>1</sup> contradict a complicated alloy composition dependence of donor binding energies in alloys such as that deduced by Craford *et al.*<sup>23</sup> for S in  $\text{GaAs}_{1-x}\text{P}_x$  from galvanomagnetic measurements using hydrostatic pressure.

We would like to close this discussion of the experimental results with a word of caution regarding the chemical nature of some of the impurities we have discussed. The  $n$ -type conductivity of the samples used here seem to be dominated by the intentional ( $n \sim 10^{17} \text{ cm}^{-3}$ ) Te doping. It is only on this basis that certain transitions have been associated with Te. Based on experience with GaP, S could exist in the alloy with nearly the same concentration. Thus the exciton associated with Te could actually be bound to S (identical binding energies in GaP). A number of other electrically active impurities such as C, Si, and N are expected in the alloy as a result of the crystal-growth process used. The conclusions stated in this paper stand independent of the chemical nature of the impurities discussed, although we have offered the most logical assignment for each transition when possible.

#### B. Curvature in the Alloy Composition Dependence of the $\Gamma_{8v}$ - $X_{1c}$ Energy Gap

We have noted in the foregoing discussion that the  $\text{In}_{1-x}\text{Ga}_x\text{P}$   $\text{Te}_0$  exciton energy, extrapolated to GaP, is about 7 meV too low.<sup>21</sup> It has been possible to neglect an effect of this size in a general discussion of the band structure of  $\text{In}_{1-x}\text{Ga}_x\text{P}$ . An understanding of this effect, however, can potentially provide details of the behavior of electronic states in alloys.

Logan *et al.*<sup>24</sup> have measured the alloy composition dependence of the energy of the exciton bound to neutral S donors in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  for  $0.984 < x \leq 1.000$ . They find an energy dependence given by

$$E_s^{2^\circ\text{K}} = 2.140 + 0.170x \text{ eV} \quad (3)$$

in this alloy composition range. Equation (3) and the dependence found here<sup>21</sup> for  $\text{Te}_0$  intersect at  $x = 0.945$ . One would expect a smooth transition between the slopes 0.039 (eV/unit mole fraction) and 0.170 (eV/unit mole fraction). Further, the exciton slope at  $x = 0.50$  would be most likely 0.017 (eV/unit mole fraction), the slope of the  $X$  conduction band. On the basis of these slopes we estimate that the  $\text{Te}_0(\text{S}_0)$  exciton energy deviates from a linear alloy composition dependence by a maximum of about 0.022 eV (at  $x = 0.50$ ). Approximately half of this deviation is effected within 10 mole% of GaP. It is clear that a polynomial of degree higher than two is required to describe the exciton energy vs alloy composition relationship.

Two mechanisms that can account for this curvature in the  $\text{Te}_0$  exciton energy vs alloy composition relationship are (i) local nearest-neighbor-type effects operating via the valley-orbit splitting of the exciton electron ground state; (ii) strain in the alloy operating primarily through Bloch states.

(i) The electron state of the observed  $\text{Te}_0$  exciton is a valley-orbit split singlet sublevel<sup>20</sup> of the multi-valley exciton ground state.<sup>25</sup> The magnitude of the valley-orbit splitting is sensitive to the immediate environment of the Te impurity. From purely statistical considerations one would expect one In and three Ga nearest neighbors for Te in the range  $0.6 < x < 0.8$  and four Ga nearest neighbors with  $x > 0.8$ . Thus one can understand how in the range  $0.71 < x < 0.85$ , where most of our data lie, the  $\text{Te}_0$  exciton energy could vary apparently linearly with composition. The discrete nature of this effect may be masked experimentally by the  $\text{Te}_0$  exciton linewidth. This is, of course, a local effect and thus would not be reflected in a similar behavior of the conduction-band-vs- $x$  curves.

(ii) A random replacement of Ga atoms in GaP by In atoms increases the lattice constant of the average material. On some smaller scale, however, there must be statistical variations in the In-to-Ga ratio from that determined for the average material. It seems valid to view these regions as areas with positive or negative (primarily hydrostatic) strain. An eigenstate such as the  $\text{Te}_0$  exciton ground state would then have a somewhat greater part of its wave function concentrated in regions of smaller band gap. The result is that the  $\text{Te}_0$  exciton energy in the actual alloy is decreased relative to its energy in a hypothetical strain-free alloy of the same composition. Free electrons and holes would also aggregate to lower the energy of the system. A plot of the energy gap vs  $x$  would in this case be parallel to the exciton-energy-vs- $x$  curve.

Either or both of these mechanisms provide a plausible explanation for the  $\text{Te}_0$  exciton behavior in the alloy. A similar behavior has been observed for the exciton reported to be bound to isoelectronic

N in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  by Chevallier and Rodot<sup>6,28</sup> and Logan *et al.*<sup>24</sup> The latter find that local effects are evident in the alloy composition dependence of the energy of the exciton bound to N when compared to that of the exciton bound to S. A quantitative evaluation of effects (i) and (ii) in the case of the  $\text{Te}_0$  exciton is at present not possible. However, the fact that no significant changes in donor and acceptor binding energies are observed with alloy composition (e.g., indirect pair spectra) suggests that mechanism (ii), above, is the one primarily responsible for the curvature in the  $\text{Te}_0$  exciton energy vs alloy composition relationship. This argument is consistent with the conclusion of Logan *et al.*<sup>24</sup> that the alloy composition dependence of the  $\text{S}_0$  exciton reflects the X conduction-band alloy composition dependence. The relatively small shrinkage of the indirect gap in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  relative to Eq. (2) predicted by mechanism (ii) cannot be detected in the relatively broad pair luminescence bands.

In summary, the  $\text{Te}_0$  exciton energy has curvature in its alloy composition dependence. The largest curvature occurs within 10% of GaP in alloy composition. The maximum deviation from a linear alloy composition relationship is estimated as  $-22$  meV at  $x=0.50$ . We expect the indirect  $\Gamma_{8v}\text{-X}_{1c}$  band gap to exhibit approximately the same curvature. The direct-indirect conduction-band crossover, with this correction for the indirect conduction band, would be at  $x=0.73$ ,  $E_g=2.32$  eV at  $2^\circ\text{K}$ —not a significant change considering the experimental uncertainties involved.

## V. CONCLUSIONS

### Photoluminescence measurement in $\text{In}_{1-x}\text{Ga}_x\text{P}$ at

$2^\circ\text{K}$  in the  $0.45 < x < 1.00$  range of alloy composition have confirmed the location of the  $300^\circ\text{K}$  direct-indirect conduction-band crossover<sup>9,10</sup> at  $x=0.74$ ,  $E_g=2.26$  eV ( $x=0.74$ ,  $E_g=2.33$  eV at  $2^\circ\text{K}$ ). For  $x > 0.72$  the spectra were similar to those of indirect-band-gap GaP. Shallow bound exciton recombination is observed in this range. We speculate on evidence in the bound exciton data that the indirect ( $\Gamma_{8v}\text{-X}_{1c}$ ) energy gap has some concave curvature when plotted as a function of alloy composition  $x$ . The maximum magnitude of this effect seems to be on the order of 22 meV and would bring the crossover to  $x=0.73$ ,  $E_g=2.32$  eV at  $2^\circ\text{K}$ . PL spectra characteristic of direct-band-gap  $\text{In}_{1-x}\text{Ga}_x\text{P}$  were observed with  $x$  up to 0.68 (note that this composition is dependent on the binding energies of the "indirect" donors). In the intermediate range  $0.68 < x < 0.72$ , intrinsic direct recombination occurs together with indirect pair recombination. We find that shallow donor ground states associated with the X and  $\Gamma$  conduction bands seem to be tied quite rigidly to these conduction bands. No mixing of the X and  $\Gamma$  donor states has been detected. Thus significant mixing occurs over a composition range of less than  $\Delta x=0.02$ , the compositional resolution in the present measurements.

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<sup>21</sup>In detail: A least-squares linear fit of the  $\text{Te}_0$  exciton energy in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  to alloy composition gives

$$E_{\text{Te}_0}^{2^\circ\text{K}}(x) = 2.264 + 0.039x \text{ eV.}$$

This extrapolates to 2.303 eV at GaP. If we assume the difference between the indirect band gap and the "extrapolated value" of the exciton energy is similar in InP and GaP, this implies that the indirect  $\Gamma_{8v}$ - $X_{1c}$  gap in InP at  $2^\circ\text{K}$  is 2.299 eV ( $\pm 0.030$  eV). The error estimate is based on worst-case deviations of experimental data from the least-squares fit. This value lies within experimental error of the value  $2.32 \pm 0.02$  eV determined by Dumke *et al.* (Ref. 14). Because of the large extrapolation involved in the former value, the latter value has been used in Eq. (2). The possibility of a smaller nonlinear deviation of the indirect gap from Eq. (2) is discussed in Sec. IV B.

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<sup>26</sup>J. Chevallier and H. Rodot report that the N-exciton binding energy extrapolated to GaP from  $\text{In}_{1-x}\text{Ga}_x\text{P}$  is lower than that observed in GaP. There is some confusion in their paper about the exciton energy in the  $0.9 < x < 1.0$  region of alloy composition. We have observed the same spectrum and find the principal exciton recombination spectral peak at 2.3125 eV for  $x = 0.990$ , and  $(dE/dx) = 0.48$  (eV/unit mole fraction) for  $0.990 \geq x \geq 0.980$  [A. Onton, T. N. Morgan, and T. S. Plaskett (private communication)]. These results are consistent with those of Logan *et al.* (Ref. 24). However, the value of  $dE/dx$  we find is considerably larger. The conclusion Chevallier and Rodot reach on the location of the conduction-band crossover, based on the spectrum attributed to a sample with composition  $x = 0.64$ , is entirely inconsistent with the results we report in this paper.

## Heliconlike Wave Propagation in Powdered Semiconductors at Microwave Frequencies\*

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Experiments on the propagation of 35-GHz microwaves in magnetically biased powdered narrow-gap semiconductors are described and their major features explained by a simple single-scattering theory derived in the paper. Attention is restricted to grains much smaller than the wavelength of the incident waves. The grains are idealized to spheres which are gyroelectric because of the applied dc magnetic field. The scattering and absorption properties of an isolated gyroelectric sphere are analyzed using an *ad hoc* assumption that, under a given normal-mode excitation, a gyroelectric sphere can be represented by an *isotropic* sphere described by the bulk permittivity associated with that excitation. This approach explains the main features of the data in terms of particle-size-dependent resonances and high-field size-independent absorption. Variations of resonance position and strength with powder grain size, size distribution, temperature, and carrier concentration are easily understood using the single-particle expressions. Low-temperature microwave transmission in InSb and InAs powders shows well-resolved Shubnikov-de Haas oscillations at field values in remarkably good agreement with theory.

### I. INTRODUCTION

We have investigated experimentally and theoretically the problem of electromagnetic wave propagation in powdered narrow-gap semiconductors in the presence of an externally applied magnetic field.<sup>1-3</sup> We report experiments carried out in the microwave region (35 GHz) on granulated high-mobility materials which exhibit a strong and striking dependence of wave-propagation properties on the applied dc magnetic field. A complete quantitative description of the data demands a rather sophisticated analysis, entailing particle-particle interactions and the effect of irregular particle shape, beyond the scope of the present work. Nevertheless

it will be shown that all observed qualitative features of the transmissivity can be explained on the basis of a simple single-scattering theory whose essentials are presented.

It is clear that the study of electromagnetic behavior of powders provides an opportunity to investigate transport properties of materials available in granular form, as well as the effect of small size on these properties. In addition, it poses a series of problems in electrodynamics and scattering theory. Understanding of this rather complex problem is therefore highly worthwhile in general. In our discussion we shall emphasize the aspects of interest to the solid-state physicist and shall endeavor, whenever possible, to emphasize the relationship