

Radiative Recombination in *n*-Type InP

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Photoluminescence spectra of relatively pure *n*-InP display several emission bands at low temperatures, with energy peaks near 1.41, 1.38, 1.34, and 1.30 eV. We report evidence that the 1.41-eV band is a direct recombination band, and that the 1.38-, 1.34-, and 1.30-eV bands are, respectively, a donor-acceptor recombination band and two weaker replicas displaced by one and two longitudinal optical phonons. With increasing temperature in the range from 50 to 70°K, the 1.38-eV band and its phonon replicas shift toward higher energy and are strongly quenched. We interpret the shift toward higher energy as due to an increasing importance of recombination of more closely spaced donor-acceptor pairs, and the quenching of the recombination band as due to increasing ionization of the donors. The dependence of the band peak energy on donor concentration agrees with the proposed process. In addition, we have studied the variation of the 1.38-eV band with excitation intensity. Saturation of this emission is observed at high intensities indicating an average lifetime of the order of  $10^{-8}$  sec at  $n=7 \times 10^{16}$  cm<sup>3</sup>. The 1.41-eV band becomes the dominant emission above 70°K. Its peak energy follows the gap variation with temperature from 2 to 300°K. It is independent of doping level and does not saturate with increasing excitation intensity. We believe that this band results from direct electron-hole recombination, and indeed the position and shape of the 1.41-eV band agree well with a calculation of the expected direct recombination emission. The calculation is based on detailed balance arguments and optical absorption data. Several other characteristics of the emission spectrum are discussed.

## INTRODUCTION

PHOTOLUMINESCENCE and absorption of high-purity InP have been examined by Turner and Petit<sup>1</sup> and Turner *et al.*<sup>2</sup> The many similarities between GaAs and InP, both in emission and absorption, were pointed out.<sup>2</sup> Recently a revision of the interpretation of the GaAs emission spectrum was suggested.<sup>3</sup> It is to be expected that insight concerning basic elementary radiative processes may be gained by comparative study of similar compounds. This was the main motivation of this work.

## EXPERIMENTAL NOTES

Measurements were performed at temperatures ranging from 2 to 100°K in a continuous flow Dewar. In order to be sure that localized heating was not important, spectra were taken with the samples immersed in He, H<sub>2</sub>, and N<sub>2</sub>. These spectra agreed with the ones obtained in the flow Dewar at the same temperatures. Excitation was from a cw He-Ne laser operating at 6328 Å with a maximum power output of ~200 mW. The experimental arrangement has been described earlier.<sup>4</sup> Resolution was always better than 1 meV. When necessary, resolution of 0.1 meV was used. The spectrograph was calibrated by means of the laser lines whenever needed.

<sup>1</sup>W. J. Turner and R. S. Petit, *Appl. Phys. Letters* **3**, 102 (1963).

<sup>2</sup>W. J. Turner, W. E. Reese, and R. S. Petit, *Phys. Rev.* **136**, A1467 (1964).

<sup>3</sup>R. C. C. Leite and A. E. DiGiovanni, *Phys. Rev.* **153**, 841 (1967).

<sup>4</sup>R. C. Leite, J. E. Ripper, and P. A. Guglielmi, *Appl. Phys. Letters* **5**, 188 (1964).

## EXPERIMENTAL OBSERVATIONS

The photoluminescence spectrum of high-purity InP at liquid-helium temperatures as observed by Turner and Petit<sup>1</sup> consisted of a sharp line about 3 meV wide at 1.4165 eV and a series of broader lines with energies around 1.38, 1.34, 1.30, and 1.24 eV. The 1.4165-eV line was assigned to the free exciton. It displayed a complex structure which could not be explained by the

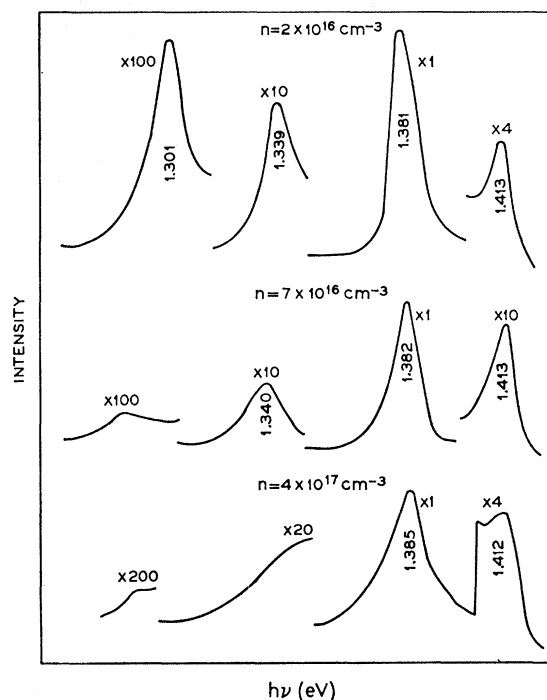


FIG. 1. Emission spectra at the absorption edge for three different donor concentrations. (2°K, scale linear in intensity.)

free-exciton hypothesis. The remaining emission bands were ascribed to recombination in a shallow impurity level with emission of 0, 1, 2, ... phonons. Our samples did not show the sharp line. They did however display in their emission spectra a high-energy band about 10 meV wide with a peak energy at 1.4135 eV at 2°K as shown in Fig. 1. This band had a width comparable to its counterpart in GaAs<sup>5</sup> and in every respect behaved similarly. Besides this band our samples showed the same series of emission bands with energies near 1.38, 1.34, and 1.30 eV. The peak frequency and relative intensities of these three bands varied with carrier concentration, intensity, and temperature. The energy separation between these peaks is approximately equal to the longitudinal optical phonon energy as measured from reststrahlen data by Newman.<sup>6</sup> This suggests that the 1.34- and 1.30-eV bands are phonon replicas of the 1.38 band, as proposed by Turner and Petit.<sup>1</sup> The fact that the energy spacing between the no-phonon emission and the two-phonon emission is not exactly twice that between the no-phonon and one-phonon bands does not invalidate this assignment. This is because phonons participating in the one-phonon process have to conserve momentum with the photon and the impurity involved. This restricts such phonons to a narrow range near  $k=0$  when the impurity involved does not alter substantially the mechanical properties of the lattice. When two or more phonons are involved in the emission process, momentum may be conserved among the phonons themselves, thus increasing the energy range of the participating phonons.<sup>7</sup>

The measured free-carrier concentration at room temperature ranged from  $2 \times 10^{16}$  to  $3 \times 10^{17}$ . The impurities which gave rise to the free electrons were not identified, and the state of compensation of the impurities was not known. We shall presume, as usual, that the room-temperature carrier concentration is a reasonable measure of the donor concentration and that the acceptor concentration does not vary from sample to sample in the same proportion as the donor concentration.

The magnitude of the integrated light intensity of the phonon replicas decreases with increasing carrier concentration as shown in Fig. 1. In this concentration range, banding of hydrogenic donor states is expected to set in so that this behavior is not surprising. These shallow states cannot be represented any more by a single  $k$  vector wave function, but rather by a superposition of wave functions with different wave vectors. Thus the  $k$  selection rule breaking down as banding increases would imply a lesser content of phonon-assisted processes.

Figure 1 also shows that the 1.38-eV band shifts towards higher energies as the carrier concentration increases whereas the 1.41-eV band does not shift appreciably. The temperature was 2°K and excitation was at moderate intensity levels, so that no appreciable saturation effects occurred.

Figures 2 and 3 show the evolution of the edge emission spectrum as the temperature increases for an *n*-type sample with room-temperature carrier concentration of  $7 \times 10^{16}$  cm<sup>-3</sup>. These spectra were obtained at a moderate constant excitation intensity. From 2 to 50°K there is no appreciable change of the relative intensities of the emission bands even though an overall decrease in intensity is observed. This is illustrated in Fig. 3. A sudden decrease in the 1.38-eV band and its phonon replicas occurs from 50 to 80°K. In GaAs the second band is quenched in the same way but at lower temperatures. Simultaneously with this, the 1.38-eV band has its energy peak shifted towards higher energies, a feature observed also in Cu-doped GaP<sup>8</sup> and lightly doped *n*-GaAs.<sup>3</sup> In GaAs, the high-energy band is enhanced when quenching of the second band occurs. This effect is not appreciable in InP. At higher temperatures the 1.41-eV band is the only emission present.

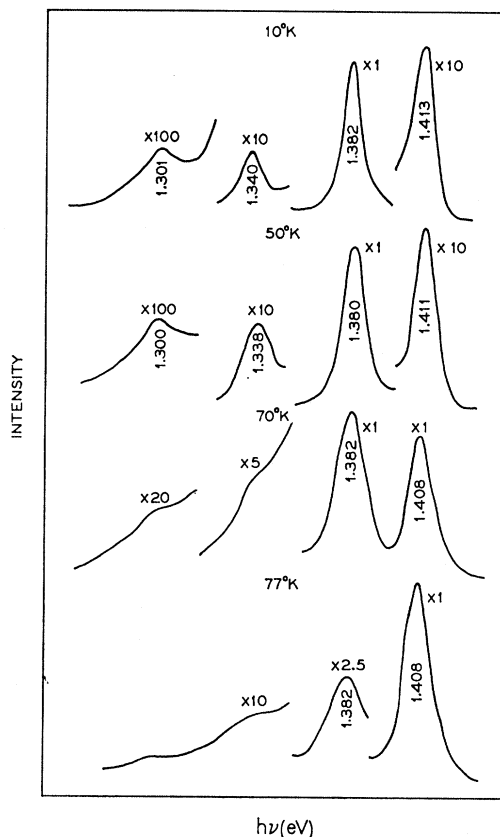


FIG. 2. Evolution of the emission spectrum with temperature.

<sup>8</sup> M. Gershenson, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik (to be published).

<sup>5</sup> R. C. C. Leite (to be published).

<sup>6</sup> R. Newman, Phys. Rev. **111**, 1518 (1958).

<sup>7</sup> R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters **17**, 538 (1966).

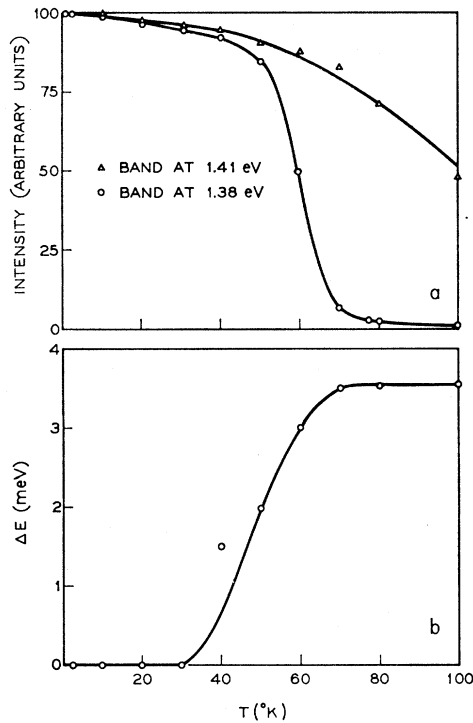


FIG. 3. (a) Variation of the integrated light intensity with temperature for emission bands at 1.41 and 1.38 eV. Both band intensities are normalized to their value at 2°K. (b) Energy peak shift with temperature of the 1.38-eV emission band as referred to its value at 2°K. Correction due to the energy gap variation with temperature is included.

Figure 3 shows the energy peak variation with temperature for the 1.38-eV band and its simultaneous quenching. The emission peak frequency change is expressed as the difference between its value at 2°K and that at temperature  $T$ . Correction due to the energy gap variation with temperature is included, this variation being derived from the 1.41-eV band which seems to follow the energy gap. The lower-energy bands at 1.34 and 1.30 eV shift simultaneously with the 1.38-eV band, supporting the assignment of phonon satellites.

Figure 4 shows spectra observed at 2°K from the same sample at several levels of excitation intensity. Figure 5 gives the integrated light intensity in the first and second bands as a function of excitation intensity. From this figure it can be noticed that the second band displays a slight shift towards higher energies as the excitation intensity is increased. The 1.38-eV band saturates at high excitation intensities, whereas the 1.41-eV band is enhanced. This was not observed in GaAs.

Figure 5 seems to indicate that enhancement of the 1.41-eV line occurs simultaneously with the saturation of the 1.38-eV line. We believe that this is rather a coincidence since in different carrier concentration materials enhancement of the high-energy peak some-

times occurs before any saturation of the 1.38-eV band is observed.

A surprising result was that at very high intensities the 1.38-eV band is considerably more efficient than its equivalent at 1.49 eV in GaAs. The high-energy bands in both materials have comparable quantum efficiencies at moderate excitation intensities but at higher excitation levels the 1.41-eV band in InP displays an appreciable increase in quantum efficiency. It seems then that InP is a better material for the manufacture of Wilson-type diodes,<sup>9</sup> since in these devices recombination occurs in the lightly doped  $n$ -side of the junction.

#### DONOR-ACCEPTOR PAIR RECOMBINATION

It was proposed recently that donor-acceptor pair recombination might account for the 1.49-eV emission band observed from lightly doped  $n$ -type GaAs.<sup>3</sup> This band behaves in many respects similarly to the 1.38-eV band described here. As in the case of GaAs, the discrete portion of the donor-acceptor pair spectra is not expected to be easily observed in InP since hydrogenic donors have very small binding energies. Pair

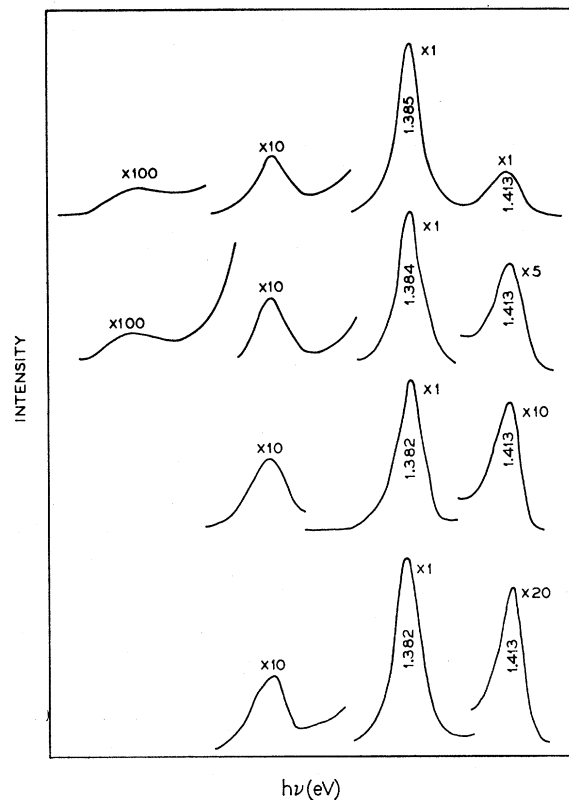


FIG. 4. Evolution of the emission spectrum with excitation intensity for four different excitation levels. Excitation increases from the bottom. (2°K, for excitation level refer to Fig. 5.)

<sup>9</sup> D. K. Wilson, Appl. Phys. Letters 3, 12 (1963).

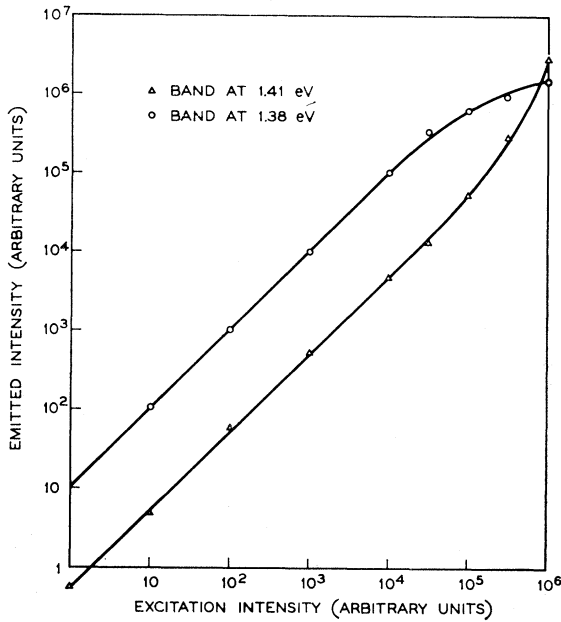


Fig. 5. Emitted peak intensity as a function of excitation intensity for the bands at 1.41 and 1.38 eV.

lines corresponding to those observed from isolated pairs in GaP<sup>10</sup> would have the related donor state above the conduction band in InP, and hence, the donor would be permanently ionized.

The recombination energy  $h\nu$  due to donor-acceptor pair recombination is given by

$$h\nu = E_G - (E_A + E_D) + e^2/\epsilon r, \quad (1)$$

where  $E_G$ ,  $E_A$ , and  $E_D$  are the gap energy and the acceptor and donor ionization energies, respectively. The last term is the Coulomb interaction energy between the two impurities considered and  $r$  is their separation distance. The energy peak shift illustrated in Fig. 1 for the 1.38-eV band is accounted for by the increase in the average Coulomb energy term of Eq. (1). The calculated increment in Coulomb energy from  $2 \times 10^{16}$  to  $4 \times 10^{17}$  cm<sup>-3</sup> donors at their most probable separation distance is  $\sim 3$  meV, when the acceptor concentration  $N_A$  is assumed to be somewhat smaller than the donor concentration. This value of 3 meV is in good agreement with the observed shift of  $\sim 4$  meV.

The observation summarized in Figs. 2 and 3 can readily be understood from the proposed mechanism. As the temperature is increased, electrons are released from their donor sites quenching the donor-acceptor recombination rate. The released carriers may then recombine by other processes. It is also possible for some of the released electrons to find their way to other donors. As the recombination lifetime for this process increases exponentially with distance  $r$  between

the involved donor and acceptor, it is to be expected that thermal release of carriers results in a reduction of average lifetime. This is accompanied by an increase in the average Coulomb energy contribution to  $h\nu$ , which results in the observed shift of the band peak towards higher energies. This should occur simultaneously with a considerable reduction in intensity as observed.

The intensity dependence of a donor acceptor pair band can be predicted. We should expect saturation of the longer-lifetime distant pair states to occur as the intensity increases. This should result in a channeling of recombination through the closer-spaced donor-acceptor pairs, with a consequent increase in the Coulomb energy component. This effect is always observed but the magnitude of the shift varies from sample to sample. Under the assumption that the carrier concentration at room temperature is a reasonable measure of the donor concentration, the observed saturation allows for order of magnitude evaluation of the average lifetime involved in the 1.38-eV emission band. This turns out to be of the order of  $10^{-8}$  sec for the sample with a room-temperature carrier concentration of  $7 \times 10^{16}$  cm<sup>-3</sup>. This evaluation was made for a calculated photon density of  $10^{21}$  sec<sup>-1</sup> cm<sup>-2</sup> in the focused laser beam spot. The carrier diffusion length and the light penetration depth were taken as  $\sim 1 \mu$ . At this point it is interesting to note that under identical conditions no saturation is observed in the 1.49-eV band of GaAs, which in every other respect has a similar behavior to the 1.38-eV band of InP. This indicates that the lifetime for donor-acceptor pair recombination in GaAs is considerably shorter than in InP for equal dopings. This suggests that in InP the donor wave functions are more localized than in GaAs, hence implying deeper states. This agrees qualitatively with the observation that the ionization energy deduced from the temperature quenching of the second band is larger in InP than in GaAs.

#### DIRECT ELECTRON-HOLE RECOMBINATION

Prior studies of the role of the exciton in absorption-emission spectra in GaAs may be summarized as follows. Absorption measurements made by Sturge<sup>11</sup> on GaAs showed a maximum in the absorption edge which at 90°K is at  $\sim 1.508$  eV and at 4°K is at 1.517 eV. Sturge ascribed this peak to the formation of free excitons. Nathan and Burns<sup>12</sup> observed in emission a peak at  $\sim 1.514$  eV at 4°K. They assigned this emission to the free exciton and proposed that the discrepancy in energy was due to a questionable correction made by Sturge. Sarace *et al.*,<sup>13</sup> by means of the principle of detailed balance, obtained very good agreement be-

<sup>11</sup> M. D. Sturge, Phys. Rev. **127**, 768 (1962).

<sup>12</sup> M. I. Nathan and G. Burns, Phys. Rev. **129**, 125 (1963).

<sup>13</sup> J. C. Sarace, R. H. Kaiser, J. M. Whelan, and R. C. C. Leite, Phys. Rev. **137**, A623 (1965).

<sup>10</sup> D. G. Thomas, M. Gershenzon, and M. Kowalchik (to be published).

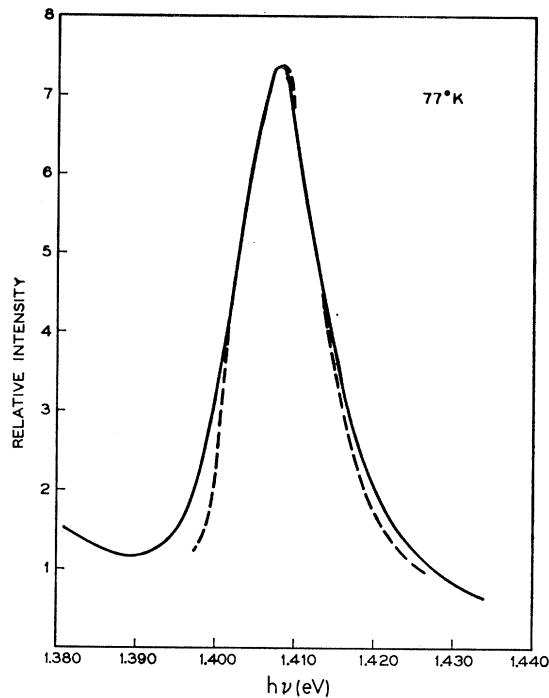


Fig. 6. Emitted band of  $\sim 1.41$  eV at  $77^\circ\text{K}$ . The observed band is the solid curve and the calculated is the dashed one.

tween the high-energy electroluminescence emission band at 1.508 eV observed from lightly doped diodes at  $77^\circ\text{K}$  and Sturge's absorption data as reduced to  $77^\circ\text{K}$ . The high-energy band observed from lightly doped GaAs both in photoluminescence<sup>3</sup> and electroluminescence<sup>14</sup> shifts to 1.5115 eV when the temperature is reduced to  $4^\circ\text{K}$ . It was then concluded that the high-energy emission observed from lightly doped GaAs was due to direct electron-hole recombination. In this context, direct recombination includes free-exciton annihilation and band-to-band transitions. The 1.514-eV band observed by Nathan and Burns at  $4^\circ\text{K}$  remained unexplained.

In the case of InP we again face the same problem. Figure 6 shows the 1.41-eV emission band at  $77^\circ\text{K}$ . The experimental band is given by the continuous

<sup>14</sup>R. C. C. Leite, J. C. Sarace, A. Yariv, D. H. Olson, R. G. Cohen, and J. M. Whelan, *Phys. Rev.* **137**, A1583 (1965).

line and the dashed spectral curve is calculated from the principle of detailed balance under the assumption that at such temperature phonon-assisted transitions are unimportant. The relative intensity of the calculated curve is then proportional to the product of the absorption coefficient  $\alpha$  at a photon energy  $\epsilon$  and the black-body distribution function,

$$\frac{\epsilon^2}{e^{\epsilon/kT} - 1}.$$

The Turner, Reese, and Petit<sup>2</sup> absorption data were used, as no significant change in  $\alpha$  is expected in the doping range concerned here. In Fig. 6 it was necessary to displace the calculated curve  $\sim 2$  meV towards higher energies. This was also true for similar trial at  $4^\circ\text{K}$ . Existing uncertainties in absorption data can account for such a discrepancy. The almost perfect agreement between the calculated and the observed emission band is strong evidence for direct electron-hole recombination in InP. Many characteristics of this emission support this view. Its temperature, intensity, and doping dependence are consistent with direct electron-hole recombination. Nevertheless, if this view is to be retained, the 1.4165-eV sharp emission observed by Turner and Petit<sup>1</sup> and Turner, Reese, and Petit<sup>2</sup> remains unexplained.

## CONCLUSION

Photoluminescence of *n*-InP has disclosed two radiative recombination mechanisms. These mechanisms seem to be basically different as the two emission bands have completely different behavior with changes in temperature, doping, and excitation intensity. The higher-energy band can be accounted for by direct electron-hole recombination both in shape and general behavior. The lower band is accompanied by a few phonon replicas and its behavior with temperature, doping level, and excitation intensity can be accounted for by donor-acceptor pair recombination.

## ACKNOWLEDGMENTS

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