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Band-to-Band Radiative Recombination in Groups IV, VI, and III–V Semiconductors (II)

By

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8.1.1 Optical properties

Transmission and reflectivity measurements on GaP in the wavelength region 1 to 40 μm have been carried out by Kleinman and Spitzer [288, 289]. They observed a number of absorptions between 12 and 25 μm which they interpreted as two-phonon combination bands. Analysis of these combination bands led to the following values of the various phonons: LO = 378, TO = 361, LA = 197, TA_1 = 115, and TA_2 = 66 (all in cm^{-1}). Cherry [290] has observed a number of weak absorption bands in the range 8 to 12 μm. These are believed to be due to three-phonon processes. The five characteristic phonon frequencies assigned by Kleinman and Spitzer were used to calculate the expected absorptions due to three phonon processes and the calculated values are in reasonable agreement with the experimentally observed bands.

More accurate values of phonon frequencies have been resently obtained by Hobden and Russell [290a, 290b] from measurements of the Raman Spectra.

Early absorption measurements on GaP were those of Folbert and Oswald [291, 292] and of Welker [293].

The absorption coefficient of GaP at room temperature in the range 2.1 to 2.8 eV was measured by Spitzer et al. [294]. They interpreted their results in terms of indirect transitions near the threshold (2.20 eV) followed by direct transitions at higher energies.

Absorption measurements at room temperature were also carried out by Loebner and Poor [295]. They found that their results for values of the absorption coefficient, α, between 10 and 150 cm^{-1} can be fitted to the Macfarlane-Roberts expression. The energy gap was found to be between 2.20 and 2.21 eV, and the energy of the phonon ($k\,\theta$) assisting in the optical transitions was estimated to be 0.026 eV. But they have not given the value of the constant A in equation (13). The energy gap found by Spitzer et al. and by Loebner and Poor is practically identical. We assumed that equation (13) can be applied to the measurements of Spitzer et al. between 2.3 and 2.4 eV and determined $A = 3760$ when $E_g = 2.205$ eV and $k\,\theta = 0.026$ eV.

Gershenzon, Thomas, and Dietz [296] found that the low-temperature absorption spectra of crystals which are not highly strained contain structure in the region of low absorption coefficient ($\alpha < 10\ cm^{-1}$) near the band edge. A series of humps is clearly discernible when the square root of the absorption coefficient is plotted as a function of photon energy. Each hump is believed to correspond to exciton absorption with the simultaneous emission of a specific phonon.

A detailed examination of the absorption spectrum of GaP single crystals at the temperature of liquid nitrogen has been carried out by Gross and coworkers [297 to 301]. They find it consists of a number of absorption steps. The steps have sharp edges, while the edge of the main absorption line is not sharp. Therefore the steps are interpreted as indirect transitions from the valence band to the levels of the free exciton with the participation of phonons (indirect excitons). Gross et al. have also obtained phonon energies from their observations, but these are different from those given by Kleinman and Spitzer [288, 289].

More recently, Abagyan and Subashiev [302] have conducted a careful measurement and analysis of the fundamental absorption edge in the region 2 to 2.75 eV. They find that in the region from the edge to ≈ 2.51 eV

$$\alpha_1 \propto (h\,\nu - E_{g1})^2 \tag{102}$$

which is characteristic of indirect allowed transitions. For energies greater than 2.55 eV, experimental absorption coefficients are greater than those given by the above relation. These deviations are postulated to be due to electron transitions to the minimum of the higher branch of the conduction band. The values of $(\alpha - \alpha_1)$, in the region 2.55 to 2.7 eV, depend on the photon energy in the form

$$(\alpha - \alpha_1) \propto (h\,\nu - E_{g2})^3 \tag{103}$$

which points to forbidden indirect transitions. The energy E_{g2} corresponding to the position of the second minimum was found to be 2.51 eV. The (α, E) graph also indicates that the sharp, approximately exponential increase of α begins at energies of 2.7 eV and is presumably due to direct transitions.

The effect of hydrostatic pressure on the transmission of GaP in the region 2.2 to 2.7 eV has been measured by Zallen and Paul [303].

Data adopted here:

Absorption coefficient: Results obtained from the absorption coefficients

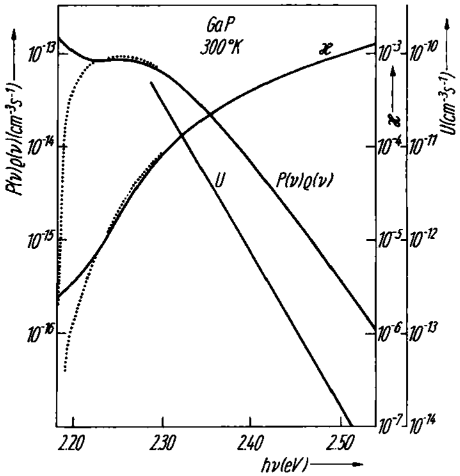


Fig. 31. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for gallium phosphide at 300 °K. The continuous curves were obtained from the absorption coefficients of [294], the dotted ones from equation (13)

measured by Spitzer et al. [294] are shown by continuous curves in Fig. 31. Results obtained from (13) with $A = 3760$, $E_g = 2.205$ eV, and $k\,\theta = 0.026$ eV are shown by dotted curves.

Refractive index: $n = 2.91$ [102].

Intrinsic carrier concentration: Calculated from (48) with the values of m_e and m_h as given in Table 1 (see Part I of this article, phys. stat. sol. **19**, 459 (1967)).

Energy gap: $E_g = 2.205$ eV at 300° K.

8.1.2 Discussion of radiative transitions

It would be noticed in Fig. 31 that the $P(\nu)\,\varrho(\nu)$ curves obtained from the data of Spitzer et al. and by equation (13) merge into one at high energies, as they should. But the Spitzer curve does not show a maximum while the dotted curve does. In this region the absorption coefficient is rather small and it is usually difficult to make accurate measurements. Presumably there is some impurity absorption superimposed on the intrinsic absorption in Spitzer's measurement which is masking the expected maximum in the $P(\nu)\,\varrho(\nu)$ curve.

We can expect another maximum at about 2.7 eV corresponding to the onset of direct transitions; but its contribution to the value of R would be relatively small.

Luminescence resulting from the flow of current through GaP diodes has been studied by a number of investigators [304, 305, 306, 295, 307 to 314]. However, the results have not been easy to analyse and the origin of the emitted radiation not unambiguously identified.

Recently a series of careful experiments have been carried out by Gershenzon and co-workers [315, 316, 296, 317 to 321] at Bell Telephone Laboratories. They have found that the spectrum observed in electroluminescence and photoluminescence is fairly complicated. Here we shall consider only those results which have a bearing on radiative recombination. Gershenzon and Mikulyak [315, 316] classify the observed luminescence peaks into four groups: band-to-band recombination, deep-donor recombination, the "sharp green line", and impurity bands.

The situation is complicated by the fact that a "sharp green line" also occurs at about the same energy as the band-to-band recombination radiation. However, it was possible to differentiate between the two by their different characteristics:

a) Recombination radiation: A weak peak (of quantum efficiency $\approx 10^{-8}$ at 1 A/cm^2 at 300 °K) lying just below the band gap at three different temperatures, 80, 200, and 300 °K, was observed in the diffused Zn–Si diodes (see Fig. 32). The peak changes its position with temperature in the direction qualitatively

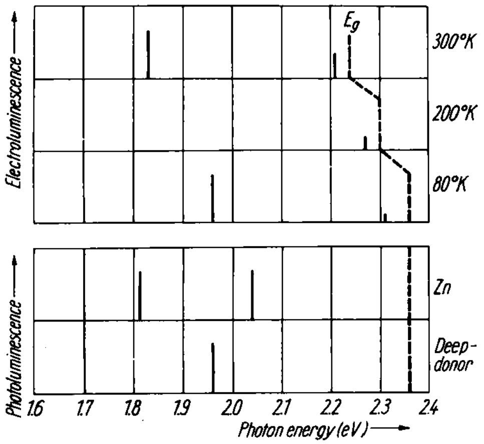


Fig. 32. Forward-bias electroluminescence of a zinc-diffused GaP diode prepared from an n-type (silicon-doped) crystal grown in a graphite container. The deep-donor emission and the band-to-band recombination peak are evident. Photoluminescence spectra of uniformly zinc-doped samples and of undoped samples containing the deep donor are shown for comparison. The band gap, E_g, is indicated at each temperature (Gershenzon and Mikulyak [316])

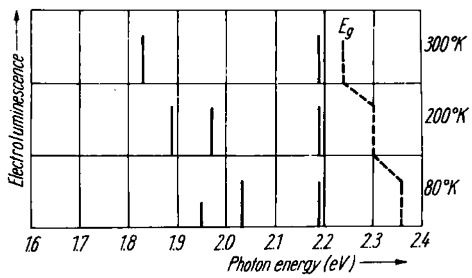


Fig. 33. Electroluminescence of zinc-diffused GaP diode prepared on n-type (sulphur-doped) floating zone crystal (Gershenzon and Mikulyak [316])

expected. Also its efficiency increases with temperature as is frequently the case with radiative recombination.

b) "The sharp green line": A sharp green line is observed at 2.18 eV (see Fig. 33). Its nature was different from all the other bands observed by Gershenzon and Mikulyak. It is far narrower than any other peak in electroluminescence or photoluminescence; its width is roughly two to four times kT in contrast with ≈ 0.2 eV widths of other bands. The band center does not shift with temperature from 20 to 500 °K. The peak is not observed at all in the diffused Zn–Si diodes prepared directly from crystals grown in graphite boats. In fact, this is the reason that the band-to-band recombination could be observed in these diodes.

Since this line is narrow and it does not shift in frequency with temperature, and its intensity does not decrease abruptly as the band gap approaches its photon energy, the emission probably arises from a fairly localized level which is well shielded from the host lattice.

The efficiency of recombination radiation in GaP has been investigated by Grimmeiss and Scholz [322].

Recombination radiation emitted from point-contact GaP diodes under conditions of reverse bias has been observed by Gorton et al. [323]. The energy of the radiation was observed to be between 1.96 and 2.19 eV, with a peak density at 2.12 eV. The maximum energy 2.19 eV corresponds closely to the minimum energy gap between the conduction and valence bands.

8.2 Gallium arsenide

Gallium arsenide is a semiconductor with many interesting properties and it has been studied quite extensively since the III–V compounds were first described by Welker [324]. A recent article by Oliver [325] gives a brief account of the preparation, physical properties, and the most important applications of gallium arsenide. A more complete review has been given by Hilsum [326].

8.2.1 Optical properties

The reflection spectrum of GaAs has been well investigated. Measurements in the infra-red have been made by Picus et al. [327] and by Hass and Henvis [106] (liquid He temperature). Piriou and Cabannes [328] have approximated the experimental reflection factor curve by fitting the parameters in the Lorentz theory equations. Observations between 1.7 to 5.1 eV have been presented by Tauc and Abrahám [209].

Morrison [329] has measured the reflectivity at nearly normal incidence from 2050 Å to 15 μm at room temperature, and has computed n and k from these data in the range 0 to 6.0 eV using the dispersion relation between the phase and the magnitude of the reflectivity. Reflectance data at higher energies (1.5 to 25 eV) have been reported by Phillipp and Ehrenreich [114]. Using this data, Davey and Pankey [330] have calculated values of n and absorption index by dispersion analysis.

Early measurements of absorption in the neighbourhood of the edge were made by Oswald and Schade [331] but they reached an absorption level of only 100 cm^{-1}. Recently Moss and Hawkins [332] have carried out measurements of absorption coefficient in the range 1.3 to 1.6 eV on single crystal GaAs. They have also compared their results with those calculated using Kane's theory [333]. In a succeeding publication, Moss [334] has also investigated the shift of the optical edge by applying an electric field.

Sturge [335, 336] has measured the absorption coefficient over the range of photon energy 0.6 to 2.75 eV, at temperatures from 10 to 294 °K. The main absorption edge was found to show a sharp peak due to the formation of excitons. Sturge finds the band gap to be somewhat larger than that found by previous workers.

Another recent investigation on the absorption coefficient of GaAs is that of Hill [337] who has studied the behaviour of the absorption coefficient, in the region of the fundamental absorption edge, with various types and levels of doping.

Turner and Reese [338] have determined optical absorption coefficients at 300 and 77 °K for samples of GaAs that were doped to concentrations comparable to those present in the n, p and p^+ regions of the GaAs injection laser.

There have also been a number of investigations on the absorption spectra in the infra-red region. Absolute absorption coefficients in the range of reststrahlen band (30 to 40 μm) have been measured by Fray et al. [339].

The infra-red absorption due to free holes in p-type GaAs exhibits three absorption bands on the low-energy side of the intrinsic absorption edge [340, 341]; n-type gallium arsenide does not show this characteristic structure, but instead exhibits a monotonically increasing absorption with wavelength. The same structure is found in all p-type samples and consequently the evidence is that these bands are not due to the presence of unknown impurities or lattice defects. Braunstein and Magid [340] interpret this spectrum in terms of hole transitions between various branches of the valence band of gallium arsenide. Spitzer and Whelan [342] have measured the infra-red absorption between 0.85 and 25 μm as a function of carrier absorption for n-type single-crystal GaAs. Infra-red absorption for p-type degenerate GaAs at room temperature for various hole concentrations has been studied by Kudman and Seidel [343].

The temperature dependence of the refractive index between 5 and 20 μm for GaAs has been determined by Cardona [344] by measuring the interference patterns of thin single-crystal films at several temperatures. His results show that the change is only about 0.45% for a 100° change of temperature. As the accuracy in reading the absorption coefficients from the curves is much less than this, we have not taken into account the variation of n with temperature.

The refractive index of GaAs has been measured by Marple [345] by the prism refraction method for photon energies from 0.7 eV to the band gap at three temperatures.

The temperature and pressure dependence of the index of refraction near the absorption edge has been estimated theoretically by Stern [346] and agrees well with experimental results.

Optical properties of thin films have been investigated by a number of workers [347, 348, 115, 330].

Data adopted here:

Absorption coefficient: The curves given by Sturge [336] at 21, 90, 185, and 294 °K were read.

Refractive index: $n = 3.63$ (Stern [346]).

Intrinsic carrier concentration: Calculated from (48) using data given in Table 1 (see Part I, phys. stat. sol. **19**, 459 (1967)).

Energy gap: Sturge [336].

The results at 21, 90, 185, and 294 °K are shown in Fig. 34 to 37 and in Table 2 (see Part I, phys. stat. sol. **19**, 459 (1967)).

8.2.2 Discussion of radiative transitions

Braunstein [349] observed a radiation from GaAs diodes which had a peak at 1.10 eV at room temperature and at 1.19 eV at 77 °K. The origin of this radiation was not clear and Braunstein pointed out the difficulty in attributing this radiation to the recombination of holes and electrons as the energy gap is considerably larger.

The recombination radiation in GaAs has been observed by Nathan and Burns [350]. Optical injection of carriers was used. A typical spectrum observed by them at 4.2 °K is reproduced in Fig. 38. Four lines are observed. The most intense line B_1 occurs at a photon energy of 1.4919 ± 0.0005 eV (22.4 meV below line A). Line B_2 is at a photon energy 36.4 ± 0.5 meV below line B_1. This energy separation is very close to the value of the LO phonon energy obtained from reststrahlen band measurements [339] (36.4 meV) and from tunnel diode measurements [351] (34.9 meV). The energy separation between B_2 and B_3 is 37 ± 2 meV and line B_3 appears to arise with the emission of two LO phonons.

As the sample temperature is increased above 4.2 °K the intensity pattern of Fig. 38 changes rapidly with decrease in the intensity of the series B, and by 40 °K they are too weak to observe, only line A remains.

Fig. 39 shows line A at 77 °K of a typical crystal grown in an O_2 atmosphere. The line occurs at a photon energy of 1.5143 ± 0.0005. (The uncertainty is

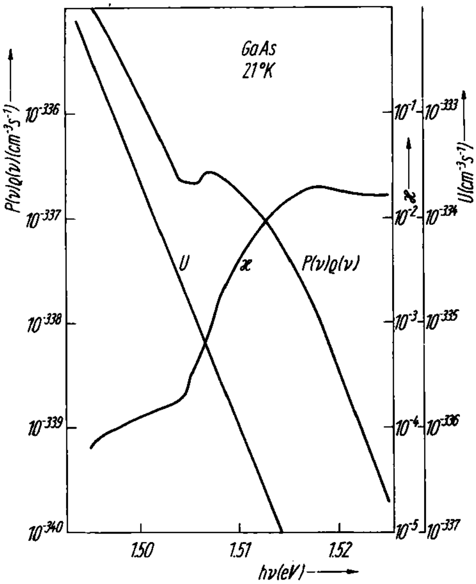


Fig. 34. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for gallium arsenide at 21 °K

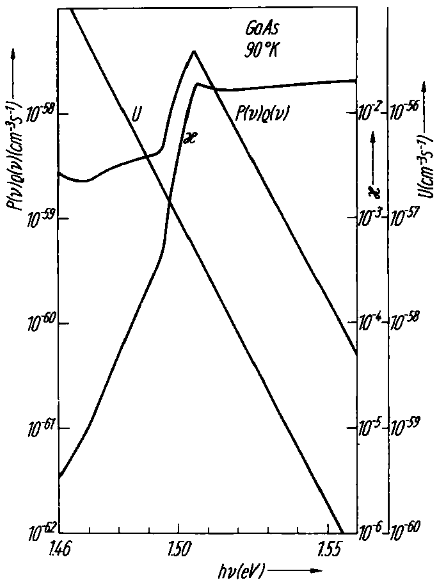


Fig. 35. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for gallium arsenide at 90 °K

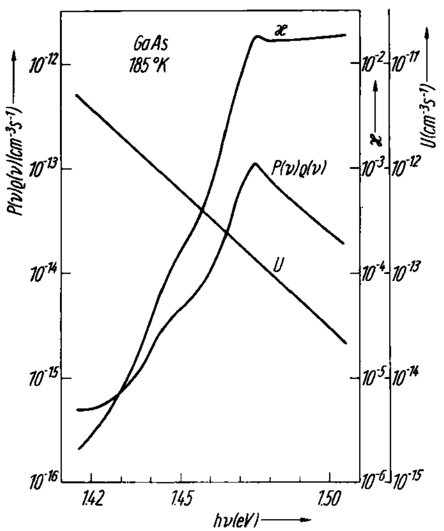


Fig. 36. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for gallium arsenide at 185 °K

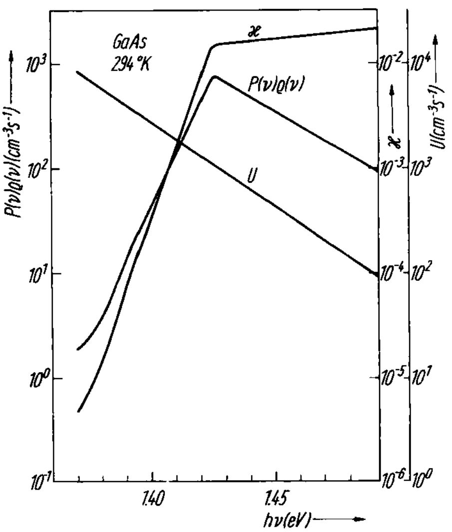


Fig. 37. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for gallium arsenide at 294 °K

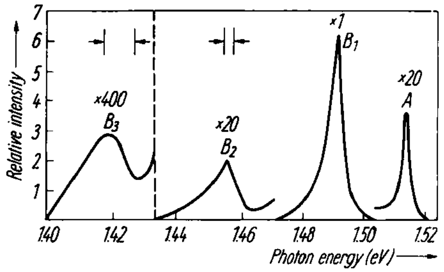


Fig. 38. Emission spectrum of a gallium arsenide crystal at T = 4.2 °K. The scale is linear in wavelength (Nathan and Burns [350])

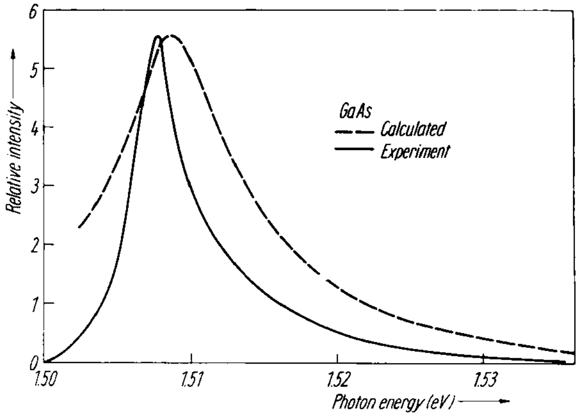


Fig. 39. Recombination radiation in gallium arsenide at 77 °K. The solid curve represents the observations of Nathan and Burns [350], the dashed curve was calculated as explained in the text

due to a small variation of the position of the line from sample to sample.) The dashed curve is the calculated one and was obtained as follows: $P(\nu)\,\varrho(\nu)$ was obtained from Sturge's [336] data at 90 °K and this was shifted to the higher energy side by 0.0025 eV corresponding to the difference in the energy gaps at 90 and 77 °K. The maxima of the two curves are seen to differ by a small amount ($\approx$ 0.0007 eV) which is of the same order as the experimental uncertainty, and it would be reasonable to disregard this small difference. But there is a marked difference in the shapes of the two curves. Even if the two maxima are made to coincide, the experimental curve is much steeper than the theoretical one.

Recently Sarace et al. [352] have measured the spontaneous injection luminescence of forward biased GaAs p–n junctions with special emphasis on the reduction of spectral distortion. Principal sources of distortion are self-absorption and internal reflection within the GaAs. The radiation observed by them together with the calculated one is shown in Fig. 40. The agreement is seen to be satisfactory.

Recombination radiation of GaAs on excitation with fast electrons has been observed by

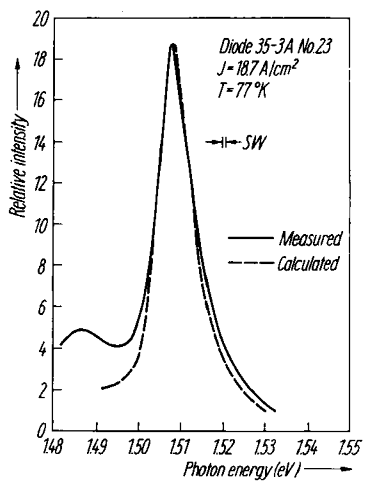


Fig. 40. Comparison of the calculated and observed radiation from gallium arsenide at 77 °K by Sarace et al. [352]

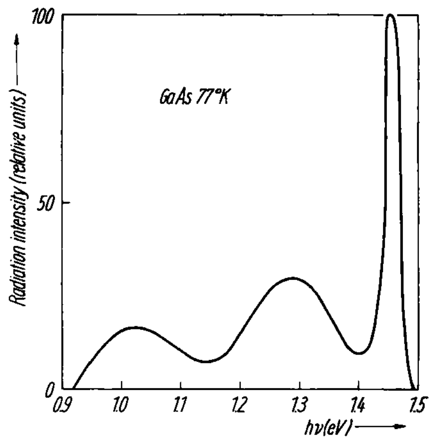


Fig. 41a. Recombination radiation from a gallium arsenide p-n junction at 77 °K observed by Nasledov et al. [353]

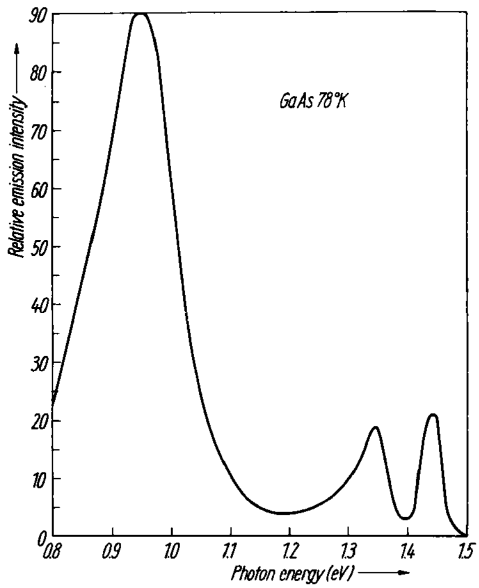


Fig. 41b. Recombination radiation from a gallium arsenide p-n junction at 78 °K observed by Pankove and Massoulie [354]

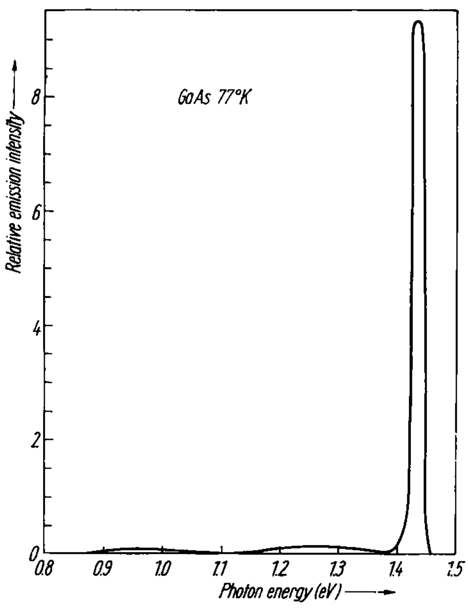


Fig. 41c. Recombination radiation from a gallium arsenide p-n junction at 77 °K observed by Keyes and Quist [356]

Basov and Bogdankevich [96]. n-type GaAs was irradiated with a beam of electrons of approximately 0.6 MeV energy, obtained from a linear accelerator.

In recent years the electroluminescence and photoluminescence spectrum of GaAs has been studied by a number of workers. In the following we discuss the important features in the spectrum and their possible origin.

Nasledov et al. [353] produced excess carriers by pulse injection through a p–n junction. The spectrum observed by them at 77 °K is shown in Fig. 41a.

The spectrum has three maxima, one at 1.47 eV and two others at smaller energies ($\approx$ 1 eV and $\approx$ 1.3 eV).

Pankove and Massoulie [354, 355] studied the injection luminescence from a forward biased p–n junction at three temperatures (4.2, 78, and 300 °K). Their spectrum at 77 °K is shown in Fig. 41 b.

Observations on an appropriately diffused GaAs diode biased in the forward direction made by Keyes and Quist [356] are reproduced in Fig. 41 c. From absolute measurements of the emitted radiation intensity, these investigators also found that at 77 °K these diodes may be as high as 85% efficient in the conversion of injected holes into photons of the gap energy.

It would be noticed from Fig. 41 a, b, and c that three maxima occur in all of them but their relative intensities are very much different in the three cases. This difference shows that the relative probability of the processes giving rise to the three maxima is a sensitive function of the conditions of the experiment. Similar results have been obtained by other workers [357, 358, 359]. At first the 1.47 eV emission was thought to be the intrinsic recombination radiation of GaAs [353], but later evidence appears to indicate that it is not so.

We may note that the radiation emitted at or near the band gap, as reported by different workers, is 1.44 to 1.50 eV at liquid nitrogen temperature. Assuming that these differences are not due to measurement error, they could be explained [360] in several ways:

a) The energy gap varies slightly from diode to diode because of crystal strains caused by impurities, dislocations, or stresses produced by junction formation.

b) Certain impurities in the crystals produce states near the band edges which tend to smear the band edges and reduce the gap.

c) Exciton formation may be favoured in some crystals but not in others.

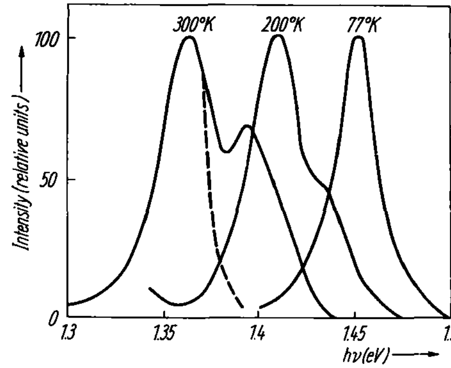
The above processes may be important in explaining some of the differences in the energy and linewidth of the radiation observed by different workers.

In 1962 stimulated emission from forward biased GaAs diodes was observed for the 1.47 eV line at 77 °K by Hall et al. [63], Nathan et al. [64], and Quist et al. [361].

Investigations, both experimental and theoretical, have been made to determine the transition which gives rise to the 1.47 eV (77 °K) emission. This strong line occurs at an energy slightly less than the energy gap in pure material (E_g = 1.51 eV at 77 °K). Theoretical investigations of Lasher and Stern [11] show that the peak of the stimulated radiation would fall at a lower photon energy than does the peak of the spontaneous radiation, except when $T = 0$ °K.

Nasledov et al. [362] have carried out experiments on GaAs photocells with a thin diffused p-region (the thickness of the p-region was of the order of a few µm). The excess carriers were produced by electrical injection and the radiation was observed in a direction perpendicular to the plane of the p–n junction from the p-type side. The carrier recombination occurred in a region whose width was of the order of a diffusion length which was approximately equal to 1 µm, Fig. 42 shows the spectrum observed by them at three temperatures. At room temperature the recombination spectrum has two maxima; these will be called the long-wavelength and short-wavelength maxima. Only the long-wavelength maximum ($\approx$ 1.46 eV) is resolved in the 77 °K spectrum. Nasledov et al. [362, 363] believe that the radiation in the long–wavelength peak is due to transitions involving impurity centers whereas that in the short–wavelength peak is associated with direct optical transitions.

Fig. 42. Spectral distribution of intrinsic recombination radiation emitted by gallium arsenide at various temperatures. The intensity of the long-wavelength peak was assumed to be 100 relative units. The dashed curve is the spectrum taken from the n-type side (Nasledov et al. [362])



McWhorter, Zeiger, and Lax [364] believe that the emitted radiation is not due to band-to-band transitions, but probably involves transitions from donor states just below the conduction band to acceptor states just above the valence band. This is consistent with the wavelength of the emission, which is longer than that of the gap at low temperatures, and the absence of an observable shift of the spontaneous emission line with magnetic field up to 90 kG.

Nathan et al. [365, 357, 358] have observed the electroluminescence and photoluminescence of GaAs at 77 °K under controlled doping conditions. The evidence from these experiments strongly indicates that the emission seen in the diodes is due to recombination involving an acceptor center. Some of the available evidence has been reviewed by Nathan [357] from whom we quote:

"Now if we ask what is the detailed mechanism of the transition the answer is very difficult to give. One of the problems is the uncertainty as to the correct way to describe the states involved in the transition. However, we can say a few things. At low concentrations ($< 10^{17}$ cm^{-3}) band-to-band recombination is undoubtedly excluded because the energy of the transition is well below the band gap. The transition is probably between the conduction band modified by the impurities and an acceptor center. For the higher concentrations ($> 10^{18}$ cm^{-3}) the impurity bands are merged with the main bands, and it is probably most correct to speak of band to band recombination. At higher concentrations the difficulty in describing the states involved is most important. The conduction and valence band states cannot be the same as in a perfect crystal. The presence of the impurities mixes states of different k, so that the k selection rule for direct transitions does not hold. The kind of band to band transitions that occur are thus different from those ordinarily encountered. In addition the impurities affect the density of states so that the bands are not parabolic near the edge. The fact that the impurities modify the energy band edges has been demonstrated from measurements of the electro-luminescent edge emission as a function of injection current. The photon energy of the peak of the emission shifts toward higher energy with increasing current [366]. The magnitude of the shift increases with increasing impurity density in the substrate [367]. Rather than actually being a shift, what is actually occurring, is a saturation of the low-energy side of the line and an increased rate of growth of the high-energy side of the line [367, 368] as shown in Fig. 43. These effects are consistent with injection into states tailing from the band edge."

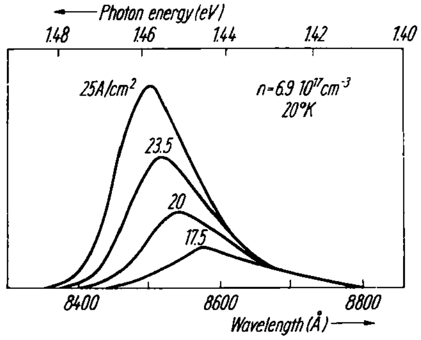


Fig. 43. Detail of the spectrum of the edge emission of a diode showing peak shift and saturation of the low-energy side of the line (from [357])

Braunstein, Pankove, and Nelson [369] have shown that the recombination spectrum depends also on the donor concentration, and that this dependence might be attributed to a concentration dependent shrinkage of the energy gap. Lucovsky and Repper [370] have studied the characteristics of the spontaneous radiation as a function of doping density in order to identify the energy levels associated with the radiative transitions. Laser action in GaAs excited by a beam of 50 keV electrons at liquid helium temperature has been reported by Hurwitz and Keyes [371].

Bagaev et al. [372] have studied the spontaneous and induced emission spectra associated with the injection of carriers through p–n junctions prepared by diffusing zinc into gallium arsenide which had a tellurium concentration ranging from 1×10^{17} to 2×10^{18} cm^{-3}. They find that their results are satisfactorily explained by radiative transitions of electrons from the conduction band which has merged with the donor levels to an impurity band formed by zinc.

The recombination radiation under conditions of low injection into a p–n junction has also been investigated by Bagaev et al. [373]. It was found that for an impurity concentration of about 10^{18} cm^{-3} the maximum of the recombination radiation shifts toward lower energies when the current is decreased.

Yunovich et al. have studied recombination radiation in gallium arsenide p–n junctions formed by beryllium diffusion [374] and by zinc diffusion [375].

Cusano [376] has determined the salient features of radiative recombination near the band edge in GaAs by electron beam excitation of donor and acceptor doped crystals ranging in impurity content from 10^{16} to 10^{20} cm^{-3}.

The laser action in GaAs is inferred from the spectral narrowing of the light emitted from p–n junctions with increasing applied current in the forward direction at 77 °K. It is reasonable to ask what role excitons play in the recombination process. Casella [377] has discussed this question. He finds that excitons (either free or bound to impurities) do not play a role in recombination process at high-current levels.

8.3 Gallium antimonide

8.3.1 Optical properties

The reflection spectrum of GaSb has been investigated by a number of workers. In the infra-red, studies have been made by several workers [327, 106, 344]. Cardona [378] has made measurements in the energy range 0.5 to 5 eV and Tauc and Abrahám [209] in the energy range 1.6 to 5 eV. Fine structure in the reflection spectrum in the energy range 3 to 5.5 eV has been observed by Lukeš and Schmidt [211].

The first measurements on absorption coefficients were those of Welker [324] and of Oswald and Schade [331], who reported results up to about 125 cm^{-1}. Roberts and Quarrington [379] carried out measurements at a number of temperatures (20, 77, 195, 249, and 289 °K). Their data goes up to $\alpha \approx 900$ cm^{-1}.

Becker, Ramdas, and Fan [380, 381] have reported measurements on p-type GaSb at several temperatures in the infra-red region as well as across the absorption edge. Their results go up to $\alpha \approx 10^4$ and span the whole of the intrinsic absorption edge. However, these measurements were made using a prism monochromator with insufficient resolution for the detection of fine structure. So later, Johnson, Filiński, and Fan [382] studied the intrinsic absorption edge using a grating instrument with good resolution at temperatures near liquid helium. Three peaks were observed which were interpreted as exciton absorption.

Edwards and Hayne [383] have obtained the refractive index in the wavelength range 1.8 to 2.5 μm from the measurements of the angle of minimum deviation (n_D) for a given wavelength of radiation as well as from reflectance measurements (n_R). The two sets of values differ: n_D values are greater than n_R values by approximately 0.2 units. No explanation of this discrepancy is at present available.

The temperature dependence of the refractive index has been determined by Cardona [344]. He finds $(1/n)\,(dn/dT) = 8.2 \times 10^{-5}$ per °C.

Data adopted here:

Absorption coefficient: At 80 and 300 °K from Becker, Ramdas, and Fan [381].

Refractive index: $n = 3.72$ (average of n_D and n_R at 1.8 μm, as given by [383]).

Intrinsic carrier concentration: Calculated from equation (48) using data given in Table 1 (see Part I, phys. stat. sol. **19**, 459 (1967)).

Energy gap : From [382] $E_{g\,80\,°K} = 0.80$ eV, $E_{g\,300\,°K} = 0.72$ eV.

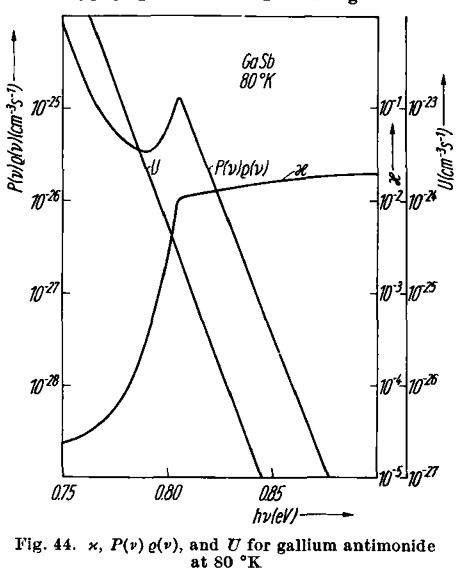


Fig. 44. ϰ, $P(\nu)\,\varrho(\nu)$, and U for gallium antimonide at 80 °K

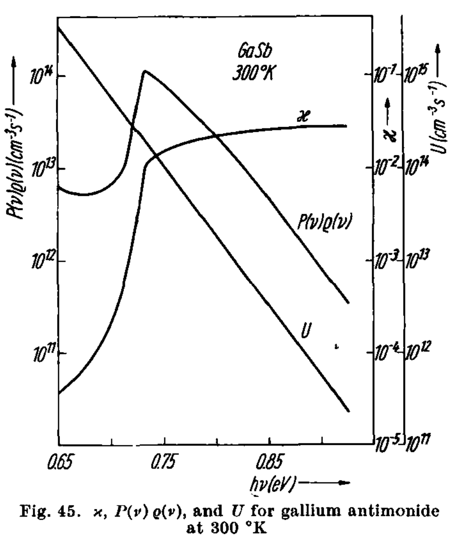


Fig. 45. ϰ, $P(\nu)\,\varrho(\nu)$, and U for gallium antimonide at 300 °K

8.3.2 *Discussion of radiative transitions*

It would be noticed from Fig. 44 and 45 that, at both temperatures, the $P(\nu)\,\varrho(\nu)$ curve does not fall continuously for energies below the energy gap. Indeed at 80 °K, below 0.79 eV it shows a marked increase with decrease in energy. This appears to indicate that the absorption data includes some contribution due to other causes.

An early attempt to observe the recombination radiation in GaSb at room temperature was made by Braunstein [349] who found a peak at 0.625 eV. The peak in Fig. 45 occurs at $\approx$ 0.73 eV and we conclude that the radiation observed by Braunstein was not due to intrinsic recombination.

Calawa [384] has recently observed the radiation emitted from forward-biased GaSb p–n junctions: At 77 °K the radiation from the diode consists of a single peak at 0.775 eV while at 298 °K it consists of a single but broader peak at 0.679 eV. At both temperatures the emission occurs at an energy below the optical energy gap of GaSb, which is 0.725 eV at 298 °K and 0.80 eV at 77 °K. Calawa found no significant line shift in both absorption measurements and measurements in magnetic fields up to 90000 G; further the radiation spectrum was found to change by the addition of a different impurity. All this evidence indicates that the observed radiation is not produced by band-to-band transitions but is probably connected with impurities.

Experiments on several GaSb diodes at high-current densities have been carried out by Deutsch, Ellis, and Warschauer [385]. They find that at 77 °K there are two emission lines, at about 0.72 eV and 0.78 eV, either or both of which may occur in the same diode. They have presented a model to explain the observed effects in terms of the band structure of GaSb.

Recently Benoit à la Guillaume and Debever [386] have observed laser action in GaSb excited by electron bombardment.

8.4 Indium phosphide

8.4.1 *Optical properties*

The optical properties of indium phosphide were first investigated by Oswald and Schade [331] and Oswald [292, 293].

Reflectance studies in the infra-red region have been made by several workers [387, 327, 106]. Cardona [388] has measured the room-temperature reflectivity of a polished n-type sample before and after etching.

The spectral emittance of indium phosphide has been measured by Stierwalt and Potter [389] in the 3 to 44 μm region at several temperatures from 77 to 473 °K. Thirteen features were observed which were attributed to two phonon processes. Using the allowed dipole-transition selection rules, values were derived for the phonon energies at the critical points.

Newman [387] has reported absorption coefficient in the vicinity of the absorption edge of n-type InP at 77 and 300 °K. Differences were found in the spectra of samples of differing origin. The effects are believed to be due to impurities.

Recently Turner, Reese, and Pettit [390] have presented very accurate optical-absorption data obtained on undoped samples of n-type InP in the region of the intrinsic edge at 6, 20, 77, and 298 °K. From this data they were able to derive the exciton energy, exciton binding energy, and intrinsic optical gap.

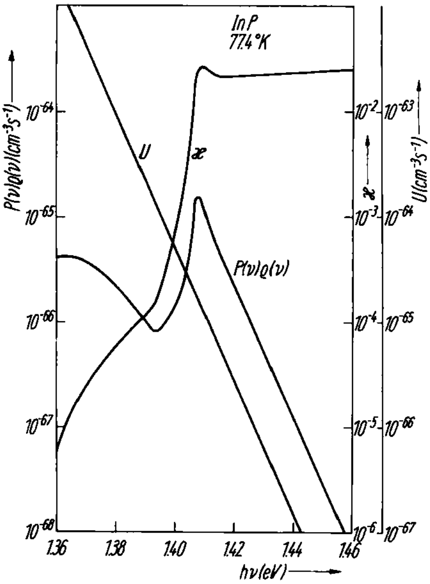


Fig. 46. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium phosphide at 77.4 °K

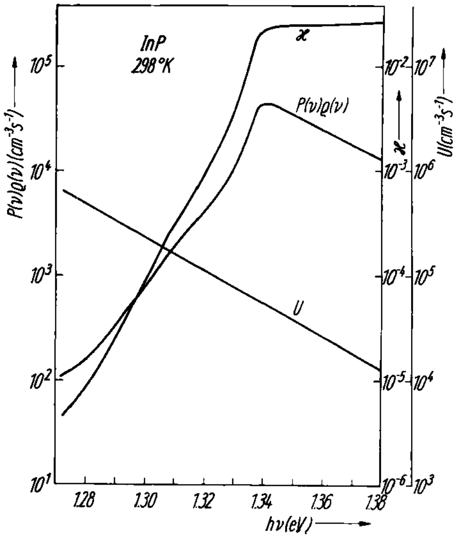


Fig. 47. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium phosphide at 298 °K

The temperature dependence of the refractive index has been investigated by Cardona [344].

Data adopted here:

Absorption coefficient: At 77.4 and 298 °K from Fig. 1 and 2 of Turner, Reese, and Pettit [390].

Refractive index: $n = 3.37$ [391].

Intrinsic carrier concentration: Calculated from equation (48) using data given in Table 1 (see Part I, phys. stat. sol. **19**, 459 (1967)).

Energy gap: $E_{g\,77\,°K} = 1.4135$ eV, $E_{g\,298\,°K} = 1.3511$ eV [390].

The results are shown in Fig. 46 and 47 and Table 2 (see Part I, phys. stat. sol. **19**, 459 (1967)).

8.4.2 Discussion of radiative transitions

An attempt to observe the recombination radiation in InP was made by Braunstein [349].

Recently Turner and co-workers [392, 390] have observed the photo-induced recombination radiation in InP. Photo-excitation of hole and electron pairs was accomplished by light of photon energies greater than 2 eV. The emitted radiation was observed from that side of the sample which received the exciting radiation. Measurements were made at 2.2, 6, and 77 °K. Their results at 77 °K are shown in Fig. 48. Line 1 is believed to be due to free exciton (and possibly some free electron–hole) recombination. The observed energy of the peak 1.409 eV is in good agreement with that expected from absorption data calculations (Fig. 47), 1.4075 eV. The small difference of 0.0015 eV is almost equal to the accuracy of measurement of the exciton peak energy, given as ± 0.0013 by Turner et al. [390].

Lines 2 and 3 result from recombination of a hole and electron at a shallow impurity with the emission of 0 and 1 optical phonons. The spacing of these

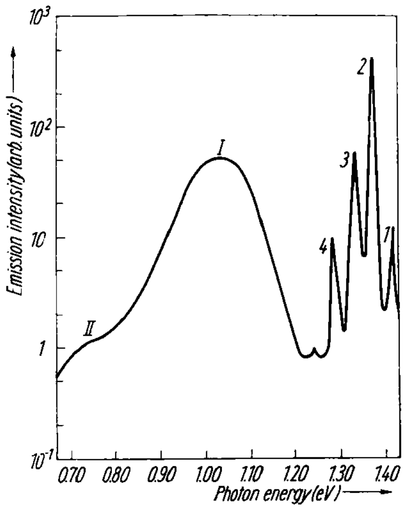


Fig. 48. Photoluminescence of InP at 6 °K observed by Turner and Pettit [392]. Net electron concentration for sample shown is 3×10^{15} cm^{-3}

lines is 0.043 eV which is exactly the LO phonon energy reported by Newman [387] from reststrahlen data.

Stimulated light emission from forward-biased InP diodes has been observed by Weiser and Levitt [393].

8.5 Indium arsenide

8.5.1 Optical properties

Reflectivity measurements on InAs have been made by several workers: Spitzer and Fan [394], Tauc and Abrahám [209] (1.7 to 5.2 eV), Lukeš and Schmidt [112] (2.3 to 2.9 eV), Greenaway and Cardona [395], and Philipp and Ehrenreich [114] (1.5 to 25 eV).

Morrison [329] has measured the reflectivity of InAs at nearly normal incidence from 2050 Å to 15 μm at room temperature. The optical constants were computed from these data in the range 0 to 6 eV using the dispersion relation.

Studies on the infra-red reflection band have been made by Picus et al. [327] and by Hass and Henvis [106]. The observed spectrum was interpreted in terms of a single classical dispersion oscillator and values of the transverse and longitudinal optical frequencies for long-wavelength vibrations were obtained.

Absorption studies in the fundamental absorption-edge region were made by Hrostowski and Tanenbaum [396], Oswald [292, 397], Stern and Talley [398, 399], Spitzer and Fan [394], Matossi and Stern [400, 401], and Nasledov et al. [402]. However, significant discrepancies exist in these results. For example, the values reported for the width of the forbidden energy gap at room temperature range from 0.31 to 0.36 eV.

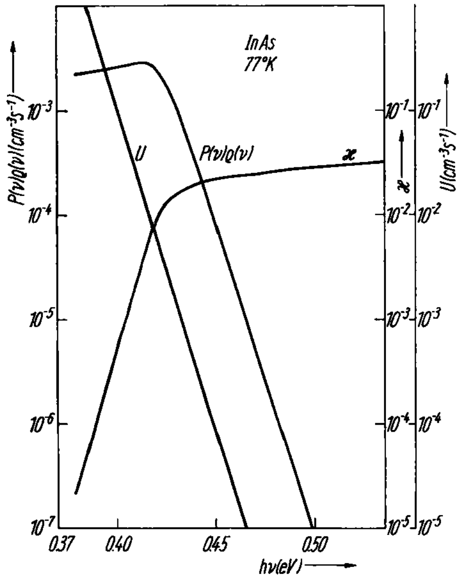
Recently Dixon and Ellis [403, 404] have measured the absorption coefficient of InAs in the fundamental absorption-edge region as a function of the impurity content. Their experiments were carried out on single crystal material of higher purity than used by most of the previous workers.

Tric et al. [405] have observed the transmission spectrum of a thin specimen of InAs at liquid hydrogen temperatures using monochromatic light modulated at 250 Hz. The simultaneous irradiation by light modulated at 175 Hz caused a slight reduction in the absorption coefficient in the region of 3.1 μm; this was attributed to laser action. Recently Melngailis [406] has observed laser action in InAs diodes.

Data adopted here:

Adsorption coefficient: a) Room temperature data from Dixon and Ellis [404]. b) For absorption coefficient at 77 °K it was assumed that the shape of the (α, E) curve remains the same as that at room temperature but it is shifted by an amount equal to the change in the energy gap. This change is 0.061 eV [404].

Refractive index: $n = 3.54$ (Morrison [329]).



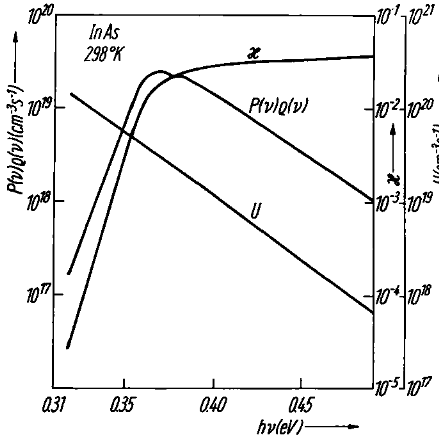


Fig. 50. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium arsenide at 298 °K

Fig. 49. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium arsenide at 77 °K

Intrinsic carrier concentration: Calculated from equation (48) using data given in Table 1 (see Part I, phys. stat. sol. **19**, 459 (1967)).

The results are shown in Fig. 49 and 50 and Table 2 (see also Part I).

8.5.2 Discussion of radiative transitions

Forward-biased InAs diodes emit an intense line of radiation at an energy slightly below the optical band-gap energy. Recently Melngailis [407] has obtained detailed results on the spontaneous emission of various InAs diodes in an effort to identify the transitions involved.

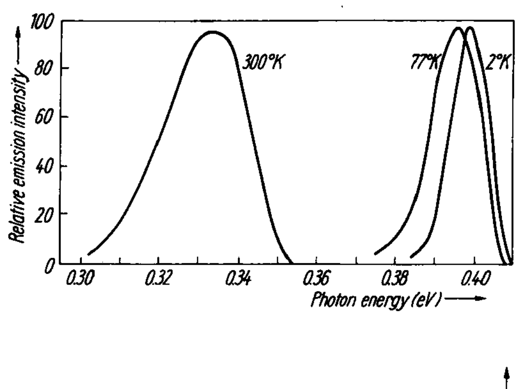


Fig. 51a. Recombination radiation from indium arsenide at different temperatures as observed by Melngailis [407]

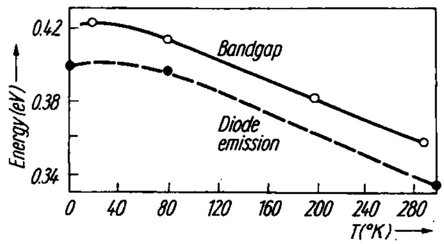


Fig. 51b. Comparison of the temperature dependence of the band gap and of the peak energy of diode emission of Fig. 51a

Fig. 51a shows the spectrum [407] at 2, 77, and 300 °K for a diode fabricated by diffusing Zn into an n-type base with a donor concentration of 2×10^{16} cm^{-3}. The intensity scale is different for each temperature. The emission line at 300 °K occurs at 335 meV or 3.70 μm and has a halfwidth of 25 meV. At 2 °K the line has shifted to 400 meV and narrowed to 12 meV. The photon energy of this line agrees closely with the energy of a line obtained in optical excitation experiments with a similar material [405, 408, 409]. Fig. 51b compares the temperature variation of the photon energy at the diode emission peak with the temperature variation of the optical band gap published by Dixon and Ellis [404] for n-type InAs of comparable purity. On the basis of two points, the diode emission line follows closely the band gap variation between 298 and 77 °K at an energy about 20 meV below the gap energy. At lower temperatures the shift of the diode emission is less than the change in the gap.

A shift of the spontaneous emission spectrum to higher energies has been observed in InAs diodes in magnetic fields up to 90 kG [410]. For the diode of Fig. 51a the energy of the peak shifts linearly with the magnetic field with a slope that is in approximate agreement with the slope expected from the lowest Landau level of the conduction band. This points to conduction band states as the origin of the transitions. The terminal states then should be acceptor levels 20 meV above the valence band, in agreement with Tric et al. [405]. This is further supported by a linear variation of radiation intensity with current.

Spectrum of the same diode at 2 °K with details of the low-energy tail is shown in Fig. 52. An additional peak occurs at 372 meV and a knee is observed at 340 meV. The first satellite 28 meV below the main peak can be explained by the recombination of an electron with the simultaneous emission of an optical phonon and a photon. The energy difference of 28 meV agrees within experimental error with the energy of 29.5 ± 0.5 meV measured for a LO phonon in InAs tunnel diodes by Hall et al. [411]. Picus et al. [327] have determined a value of 28.8 meV for the phonon from optical reflectivity data. The second weaker satellite 60 meV below the main peak corresponds to the energy of two phonons, also observed in tunnel diodes at 59 ± 0.5 meV. The emission of these phonons can be expected in InAs, since it is a strongly polar compound and has a strong coupling of electrons to the lattice.

Benoit à la Guillaume and Debever [412] have observed laser action in InAs by electron bombardment.

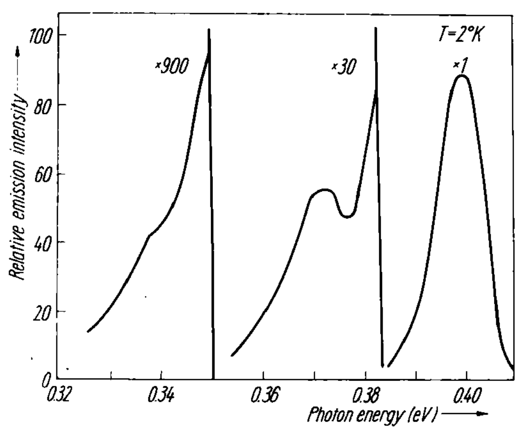


Fig. 52. Radiation from indium arsenide at 2 °K (Melngailis [407])

8.6 Indium antimonide

Among all the III–V compounds, indium antimonide has probably received the most attention.

The properties of InSb have been reviewed by Moss [413] and Hulme and Mullin [414]. The former review deals primarily with the fundamental properties of InSb while the latter one concentrates on metallurgy, diffusion, dislocations, and device applications.

8.6.1 Optical properties

The lattice absorption bands of InSb were investigated by Spitzer and Fan [415] in the wavelength range 5 to 115 μm. They found four bands at 28.2, 30, 52, and 95 μm respectively. Yoshinaga and Oetjen [416] measured the reflectivity and transmission of InSb crystals (n-type) between 20 and 200 μm. A series of detailed measurements of the absorption spectrum of high-quality single crystals of n-type InSb has been carried out by Fray, Johnson, and Jones [417, 418] in the wavelength range 15 to 130 μm and over the temperature range 4.2 to 90 °K. The positions and temperature dependence of all the principal absorption peaks could be interpreted in terms of multiple phonon interactions involving phonons with energies of 180, 156, 118, and 43 cm^{-1}.

The fundamental lattice reflection band of InSb has been measured at liquid helium temperature by Hass and Henvis [106]. By comparing the observed spectrum with that calculated using a single classical dispersion oscillator, the following optical phonon frequencies were obtained:

$$\nu_{\text{transv}} = 184.7 \pm 3\ \text{cm}^{-1}\,, \qquad \nu_{\text{long}} = 197.2 \pm 2\ \text{cm}^{-1}\,.$$

Other reflectivity measurements have been made by the following workers: Tauc and Abrahám [209] (2 to 5 eV), Morrison [329] (2050 Å to 15 μm at room temperature), Greenaway and Cardona [395] (1 to 5.5 eV), Philipp and Ehrenreich [114] (1.5 to 25 eV), Kurdiani [419] (0.22 to 17 μm), Sanderson [420] (20 to 200 cm^{-1}).

Moss, Smith, and Hawkins [421] have used transmission measurements to determine absorption coefficients over the wavelength range 1.5 to 7.5 μm and made interferometric determinations of the refractive index from 7 to 20 μm.

Absorption coefficients in the vicinity of the absorption edge in pure and n-type degenerate samples at room temperature and liquid nitrogen temperature have been measured by Gobeli and Fan [422].

The variation of the refractive index with the temperature has been studied by Cardona [344]. Kessler and Sutter [423] have reported measurements of the free-carrier absorption.

The effect of doping on the reflection spectrum of InSb in the energy region 0.35 to 1.6 eV has been investigated by Kurdiani et al. [424].

Data adopted here:

Absorption coefficient: 77 °K after Gobeli and Fan [422], 295 °K after Moss et al. [421].

Refractive index: $n = 4.01$ (extrapolated from Fig. 4 of reference [421]).

Intrinsic carrier concentration: Investigations of Hall coefficient and conductivity over a wide temperature range have been made by Howarth, Jones,

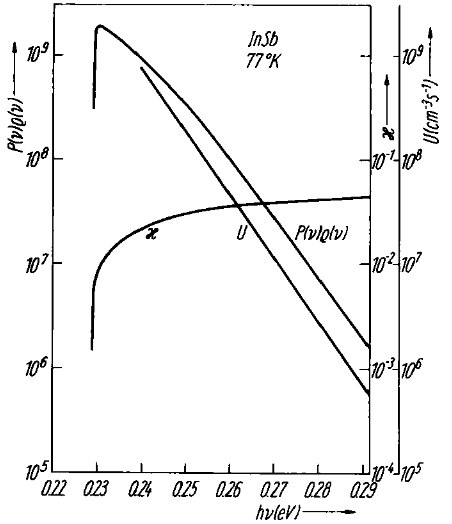


Fig. 53. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium antimonide at 77 °K

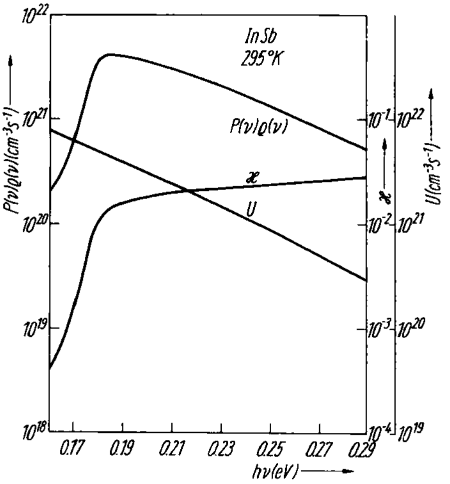


Fig. 54. $\varkappa$, $P(\nu)\,\varrho(\nu)$, and U for indium antimonide at 295 °K

and Putley [425] who give

$$n_i^2 = 1.8\times10^{22}\left(\frac{T}{290}\right)^3 \exp\left[-\frac{0.255}{k}\left(\frac{1}{T}-\frac{1}{290}\right)\right]\,\text{cm}^{-6} =$$

$$= 1.994\times10^{29}\,T^3\exp\left(-\frac{0.255}{kT}\right)\text{cm}^{-6}\,, \tag{104}$$

where kT is in eV.

Calculated values of $P(\nu)\,\varrho(\nu)$, $\varkappa$, and U are shown in Fig. 53 and 54 and other results are recorded in Table 2 (see Part I, phys. stat. sol. **19**, 459 (1967)).

8.6.2 Discussion of radiative transitions

The radiative recombination rate and the lifetime of carriers in InSb at room temperature have been calculated by earlier workers. Goodwin and McLean [426] obtained $R = 2.25\times10^{22}$ cm^{-3} s^{-1} and $\tau = 0.36$ μs. Calculations of Moss et al. [421] gave $R = 1.02\times10^{22}$ cm^{-3} s^{-1} and $\tau = 0.79$ μs.

Recombination radiation in InSb was observed by Moss and Hawkins [427, 428]. It was pointed out by Moss [98] that the spectral distribution of the radiation which is observed experimentally may differ considerably from that generated, depending on the experimental conditions. For example, in the experiments of Moss and Hawkins, the excess carriers were generated optically by highly absorbed wavelength radiation so that all the excess carriers can be considered to the generated at the illuminated surface of a thin slab and the recombination radiation was observed from the dark surface. The emitted radiation would suffer attenuation in its passage through the thin slab and would also undergo multiple reflections at the two surfaces. After making allowances for these effects, the calculated spectral distribution is shown as curve D in Fig. 55. Curve A is the measured emission curve. Allowing for the fact that the experimental curve was broadened by the low resolution which was used, the agreement between the two curves is reasonable.

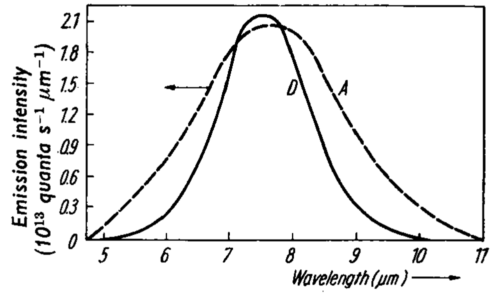


Fig. 55. Measured and expected recombination radiation distribution from indium antimonide according to Moss [98].
(A) Measured emission curve, (D) expected emission curve after taking into account the corrections

From the absolute intensity of the recombination radiation, Moss [98] estimated the percentage of recombinations which are radiative, which equals the ratio τ_B/τ_R of the bulk lifetime to the radiative lifetime, and found it to be nearly 20%.

We have mentioned above the calculated $\tau_R = 0.79$ μs. Typical measured values of τ in good quality crystals are $\approx 4 \times 10^{-8}$ s, which indicates that only $\approx 5\%$ of the recombinations are radiative. This is at variance with Moss' estimate. Landsberg [429] has suggested that this discrepancy could be explained if the short-wavelength light used to generate the excess carriers produced more than one electron-hole pair per photon. Such an enhanced quantum efficiency has been found in InSb by Tauc and Abrahám [82] and by Ivakhno and Nasledov [430].

Recently Benoit à la Guillaume and Lavallard [431, 432] have observed recombination radiation in InSb at 77 and 20 °K. Their observations are reproduced in Fig. 56.

The shape of the spectrum at 77 °K is unsymmetrical, being steeper on the low-energy side which is similar to that in Fig. 54. The maximum in the experimental curve occurs at 230.5 meV as is the case with the theoretical curve. The observed spectra may be considered to be in good agreement with the absorption data.

Recently Pehek and Levinstein [433] have carried out extensive investigations on the recombination radiation spectra of a variety of n- and p-type InSb single crystals at 300, 200, 100, and 12 °K. The emission spectra included contributions from direct band-to-band transitions, indirect phonon-assisted band-to-band transitions, transitions to flaws, and transitions bet-

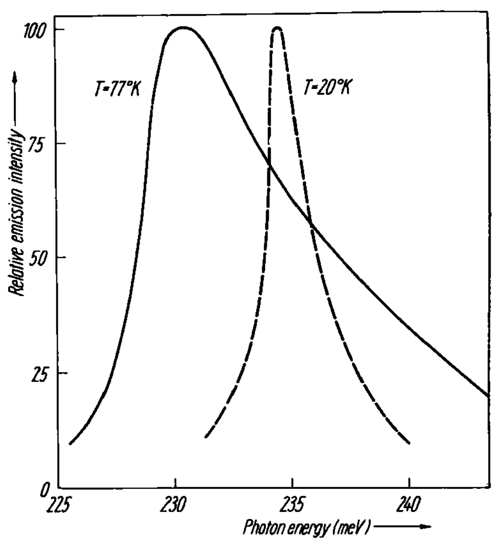


Fig. 56. Recombination radiation spectra from indium antimonide at 77 and 20 °K as measured by Benoit à la Guillaume and Lavallard [432]

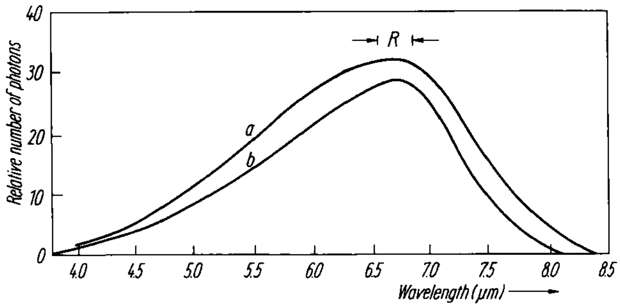


Fig. 57. Theoretical and experimental recombination emission at 300 °K (Pehek and Levinstein [433]). (a) Experimental emission adjusted for constant wavelength resolution, (b) van Roosbroeck-Shockley theory taking into account self absorption

ween localized states not thermally coupled to the lattice, the transition energies of which were larger than the band gap of InSb. Their results on the band-to-band emission at 300 °K are shown in Fig. 57.

Alferov et al. [434] have observed recombination radiation from p–n–n^+ structures in InSb at 77 °K. The spectrum was found to have an almost symmetrical shape and the maximum was located at an energy of about 0.215eV, which does not agree with the energy ($\approx$ 0.2305 eV) at which the maximum occurs in Fig. 54. This inconsistency between the absorption data and the recombination radiation data appears to indicate that the radiation observed by Alferov et al. [434] was not the "intrinsic radiation".

Vul et al. [435] have observed the recombination radiation in degenerate InSb on injection of carriers through a p–n junction. Recombination radiation from InSb under avalanche breakdown has been observed by Basov et al. [436, 437].

Investigations on the carrier lifetime have been made by Wertheim [438], Baev [439], and Gulyaeva, Iglitsyn, and Petrova [440]. Gulyaeva et al. measured the lifetime in p- and n-type InSb using steady-state photomagnetic and photoconductivity methods. They conclude that the main recombination process at high temperatures is Auger recombination.

Laser action in InSb has been observed by Phelan et al. [441] and by Benoit à la Guillaume and Lavallard [442]. Several important magnetic effects have been observed in InSb. The first of these is shift in the maser frequency which can be explained by the shift of the energy gap with magnetic field. Thus as the field is increased the excitation is transferred from one axial mode to the adjacent mode at a shorter wavelength. Another effect is the lowering of the threshold current density. The reasons for this are discussed by Lax [443].

Ivanov-Omskii et al. [444] have observed an increase in recombination radiation from single-crystal samples of p-type InSb when placed in combined electric and magnetic fields. The increase was interpreted as due to a nonequilibrium increase in charge carrier density at the sample surface resulting from the combined action of the electric and magnetic fields.

9. Comparative Discussion

The results are summarized in Table 2 (see Part I of this article, phys. stat. sol. **19**, 459 (1967)). It would be here appropriate to consider the accuracy of these quantities.

Moss, Smith, and Hawkins [421] have calculated R at 295 °K, using their own absorption data. The value they obtain is $R = 1.02 \times 10^{22}$ which may be compared with the value calculated here independently, viz. 1.03×10^{22} using the same absorption data. The good agreement shows that the absorption coefficients could be read from enlarged diagrams with resonable accuracy. The values of R depend on the accuracy of the absorption coefficients. For most entries of R, we believe the accuracy is 5% or better. Values for Si at temperatures other than 290 °K may be in error up to 15% at medium temperatures and up to 50% at low temperatures as the constant A in equation (16) appears to vary with temperature. For InAs (77 °K) the value is obtained through an approximation and could be in error by a factor of 5. The Se (hexagonal) value gives only an order of magnitude and may be in error by a factor of 10.

As regards n_i, for Si, Ge, and InSb, the values have been obtained from equations whose parameters were derived from certain experimental data and these should be of reasonable accuracy. On the other hand, for most of the other substances, n_i values have been obtained from the effective masses and are subject to appreciable uncertainties.

The results show that R and τ vary very rapidly with change in temperature. On the other hand, the recombination probability B shows only a slow change with temperature and is a convenient quantity for interpolation or extrapolation. In Fig. 58 and 59, we show $\log B$ versus $\log T$ for the various substances. Where only two points are available, these have been joined by a straight line. At least for direct gap semiconductors, there is some justification for doing so, as the theory shows that $B \propto T^{-3/2}$. However, the slope of the lines in Fig. 59 is nearer (−3) rather than the theoretically expected (−3/2). Perhaps part of

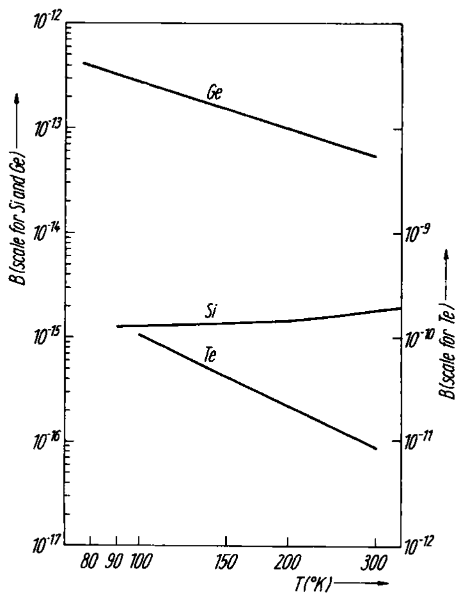


Fig. 58. Dependence of the radiative recombination probability B on temperature for Ge, Si, and Te

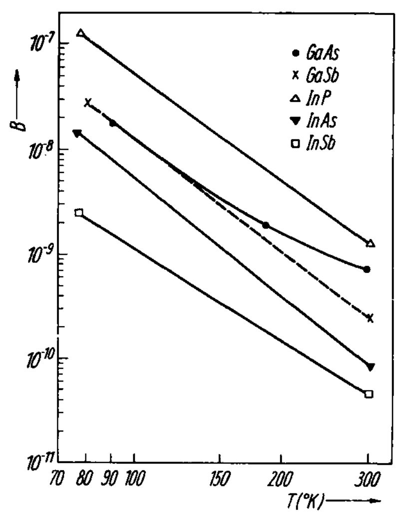


Fig. 59. Dependence of the radiative recombination probability B on temperature for the III-V semiconductors

this discrepancy could be attributed to the variation of effective masses with temperature. At intermediate temperatures these curves may be used for estimating values without too great an error.

For Ge and GaSb at $T > 400$ °K and for InSb at $T > 350$ °K, radiative recombination lifetimes would be very short. But whether or not this would be the dominant mode of recombination, depends on other competing processes.

Allowing for the approximations made in deriving the theoretical expressions for R etc., and the uncertainties in the values of the input quantities, the results given in Table 3 for the appropriate type of transition are in reasonable agreement with the corresponding results in Table 2 (Tables 2 and 3 see Part I of this article). The R-values for GaAs, GaSb, InP, InAs, and InSb (Table 3) show that for a given value of the energy gap, direct recombination is more probable than the indirect one.

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