The physics of radiative centres in GaP

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I. Introduction

An important byproduct of recent solid-state technology which has evolved in recent years is the "visible" solid-state lamp. Today, the most efficient visible solid-state lamps are fabricated from the III-V semiconductor GaP. In this article we shall review the physics and chemistry of those luminescent centres in GaP which are responsible for this efficient solid-state light emission. The physics of the luminescence consists in discovering and describing the mechanism of hole-electron recombination which leads to the generation of light. The chemistry consists in discovering which impurities in the crystals are important in the physical processes and determining how to add or remove them to produce luminescence of a particular colour. Before we discuss the physics and chemistry of luminescent centres in GaP, we shall briefly review the present status of various other means of generating light in solids.

Solids can generate visible light in several ways. For example, in incandescent lamps, electrical energy is converted to radiation by utilizing the intermediate step of heat generation. Emission of light in these incandescent lamps depends upon the temperature and size of the source (e.g. a tungsten filament). However, in electroluminescence devices, electronic energy can be converted directly into light without the added complexity of high temperature and vacuum sealing. The emission characteristics depend on the chemical composition of the host crystal and the incorporation of small amounts of special impurities. These impurities can give rise to centres which generate either useful light or non-useful light and heat; henceforth, these centres will be referred to as radiative or nonradiative centres respectively.

Electroluminescence was first observed by O. W. Lossow in 1923 [1] in SiC, who observed that light originated within the crystal near a contacting electrode and later established that this luminescence was due to radiative recombination of charged carriers injected across built-in P-N junctions. Another type of electroluminescence was observed by G. Destriau [2] in which a ZnS phosphor was suspended in a liquid and an a.c. field was applied between the two electrodes immersed in the liquid. This type of electroluminescence is believed to result from the excitation of radiative recombination centres by inelastic collisions with thermally generated charge carriers that have been accelerated to high energies under the electric field. Other methods of injecting minority carriers in semiconductors to produce luminescence have been demonstrated which do not require a P-N junction [3]. All these devices have had little success in the practical world because of either too low light output or too short life when operating at the required brightness.

In 1962, the discovery of GaAs semiconductor lasers [4] in the infrared region and demonstration of highly efficient red-emitting GaP P-N junction devices [5] [6] generated intense interest in these light-emitting devices. Since then considerable progress has been made towards the improvement of the light output and in generating various colours in these devices. These P-N junction solid-state lamps are commonly referred to as Light-Emitting Diodes or LEDs. They enjoy the same advantages over the incandescent lamps that the transistor had over the conventional vacuum tubes, in that they are extremely reliable (half-life \(\geq 10^6\) hours), efficient (as high as 12% efficiency in the red), and require low power (milliwatts) compatible with solid-state circuitry. As such, they are being widely incorporated in new equipment having solid-state circuitry to perform many of the display functions such as indicator lights and alphanumeric-readout, which have heretofore been carried out with miniature incandescent lamps, numerical indicator tubes, and neon glow lamps. Several review articles have appeared in recent years concerned with junction luminescence [7-16]. This article will therefore deal chiefly with radiative and nonradiative centres in GaP, which play a significant role in these devices operating at room temperature. Stress will be on the recent developments pertaining to radiative centres which generate high luminescent devices.

In LEDs electroluminescence is produced by forward biasing a P-N junction of the semiconductor. In principle this is a very straightforward, simple process in which holes and electrons are driven together from P and N regions (see fig. 1). Recombination of these holes...
and electrons can then result in the emission of photons with energy equal to or less than that of the energy-band gap of the semiconductor. For visible light the band gap should be greater than 1.8 eV (wavelength about 7000 Å). Recombination of the hole and electron leads to production of useful visible light or invisible light and heat. The internal quantum efficiency is the ratio of number of minority carriers (holes and electrons) that recombine radiatively (useful light) to the total number that recombine. After generation of a photon by radiative recombination, the photon may be lost by self-absorption and not escape from the solid. Thus, the most meaningful quantity in terms of efficiency, the external quantum efficiency, is the ratio of the number of externally emitted photons to the number of electrons that flow in the external bias circuit. Beside the internal and external quantum efficiency there is a concept which involves the product of the quantum efficiency and the response of the human eye which is referred to as luminous efficiency. For applications of LEDs, luminous efficiency is probably the most important property. Because of the human-eye response, diodes of external quantum efficiencies of 3% in red and 0.1% in green may look equally bright in a dark room because the eye is approximately 30 times more sensitive to green than to deep red.

Luminescent properties of the bulk material are normally studied by photoluminescence, i.e. study of the luminescence from crystals excited by light with a photon energy greater than the energy band gap. For a good LED one needs both good photoluminescent and injection efficiencies but in this review article we shall only be concerned with one of the demands, namely the photoluminescent properties of the semiconductor. An alternative excitation process is by irradiative electrons, giving rise to cathodoluminescence.

Currently P-N junction devices which emit infrared and visible light are being made from semiconductors like GaAs, GaP, GaAsP, GaAlAs, GaInP and SiC. Infrared, red, yellow and green LEDs are available today in the market. During the past ten years considerable progress has been made towards the understanding of the physics and chemistry of luminescence in these semiconductors. The semiconductors GaAs and GaP have received particular attention primarily because of the high quantum efficiencies that have been achieved. The highest external quantum efficiencies in the GaAs (infrared) and GaP (red) diodes have been reported to be 32% \(^{17}\) and 12% \(^{18}\) respectively. The essential difference in the internal quantum efficiencies in GaAs and GaP is simply related to the radiative transition probabilities in a direct and indirect band-gap semiconductor. The discussion on this aspect will be postponed until the next section.

Electroluminescence in GaAs has found its importance in the development of a continuous solid-state laser operating at room temperature \(^{19}\). Furthermore, a GaAs diode can also be used in conjunction with rare-earth-doped upconverting phosphors to generate multi-color, visible solid-state lamps \(^{80}\). In these visible lamps, infrared emission from GaAs diodes is coupled into special phosphors which are capable of converting the infrared radiation into visible light. These phosphors are known as infrared-stimulated phosphors, and

Fig. 1. Schematic representation of a semiconductor P-N junction in thermal equilibrium under zero bias (a) and under forward bias (b). \(V_D\) is the built-in potential; \(V_B\) is the applied bias; \(E_F\) is the Fermi level; \(E_A\) and \(E_D\) are the acceptor and donor levels and \(E_{QF}\) are the quasi-Fermi levels, whose energy difference is approximately equal to \(eV_B\). Minority carrier electrons (holes) are injected to the \(P\) side (N side) of the junction and there recombine radiatively or nonradiatively with the available hole (electron). (From P. J. Dean \(^{12}\).)
examples are fluorides and oxides of rare-earth elements (e.g. YF₃, YOF). The two promising features these infrared-visible converting diodes offer today are firstly that diodes have been made for the blue region of the visible spectrum as well as for the green and red regions, and secondly they provide some colour tunability in the visible region. However, these diodes have low efficiencies. The efficiency in these infrared-stimulated phosphors is low firstly because the infrared-to-visible-light conversion is brought about by absorption of two or three infrared photons to generate one visible photon, a process which has low transition probability, and secondly because the phosphors absorb about 10 percent or less of the emitted infrared radiation from the GaAs diode. Thus, to get enough brightness in these infrared-stimulated phosphors GaAs LEDs have to be driven rather hard (100 mA or more) and a rapid drop off in efficiency is observed as the excitation intensities are lowered.

Gallium phosphide on the other hand, can directly generate efficient visible light in the green, yellow and red regions of the spectrum. The luminous efficiencies of various available visible diodes are listed in Table I. The two best diodes are GaP-red and GaP-green, which respectively possess 2.4 lm/W and 3.6 lm/W luminous efficiencies. The discussion in the rest of the article will pertain to how these high luminescent efficiencies have been successfully achieved in GaP. In conclusion, we shall speculate on the quantum efficiencies achievable in the future.

### II. Band structure

Gallium phosphide possesses satisfactory electrical and crystal-growth properties as well as a large enough forbidden energy gap (2.26 eV at 300 K) for generation of visible light. However, it is an indirect band-gap semiconductor. In a direct energy-gap material (e.g. GaAs), the minimum energy of the conduction band and maximum energy of the valence band lie at the same crystal-momentum wave vector \( k \). For an indirect-gap semiconductor (e.g. GaP), the minimum of the conduction band does not lie at the same value of \( k \) as the maximum in the valence band. For comparison, the band structures of GaAs and GaP are presented in fig. 2a and 2b. Thus, for an electron in the conduction band to recombine with a hole in the valence band in an indirect semiconductor, a momentum equal to \( k = k_c - k_v \) has to be accounted for since momentum is to be conserved: \( k_c \) and \( k_v \) are the electron and hole momenta at the conduction band and valence band respectively. Because of the restriction on the crystal momentum, the intrinsic recombination probability of the electrons and holes is low. However, the recombination of electrons and holes can be greatly enhanced by addition of impurities which interact strongly with free carriers, enabling crystal momentum to be conserved through an impurity-carrier interaction. We can thus think of the impurity inducing an efficient luminescence. It is just such an impurity-induced emission which produces efficient light generation in GaP.

<table>
<thead>
<tr>
<th>Material</th>
<th>Radiative transition: direct (d) indirect (i)</th>
<th>Peak emission wavelength</th>
<th>Quantum efficiency</th>
<th>Ref.</th>
<th>Luminous efficiency (lumens/watt) for 100° best measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs₀.₁₈P₀.₈₂ (red)</td>
<td>d</td>
<td>1.84 675</td>
<td>1.3 x 10⁻⁴</td>
<td>III</td>
<td>~0.45</td>
</tr>
<tr>
<td>GaP (red)</td>
<td>i</td>
<td>1.77 699</td>
<td>12 x 10⁻³</td>
<td>V</td>
<td>~20</td>
</tr>
<tr>
<td>GaP (green)</td>
<td>i</td>
<td>1.77 699</td>
<td>12 x 10⁻³</td>
<td>V</td>
<td>~20</td>
</tr>
<tr>
<td>In₀.₂₂G₀.₇₈P (red)</td>
<td>d</td>
<td>2.17 571</td>
<td>2 x 10⁻⁴</td>
<td>IV</td>
<td>610</td>
</tr>
<tr>
<td>In₀.₂₂G₀.₇₈P (green)</td>
<td>i</td>
<td>2.22 558</td>
<td>6 x 10⁻³</td>
<td>VI</td>
<td>600</td>
</tr>
<tr>
<td>GaAs₀.₁₈P₀.₈₂ (yellow)</td>
<td>i</td>
<td>2.05 605</td>
<td>1 x 10⁻⁴</td>
<td>VII</td>
<td>~400</td>
</tr>
<tr>
<td>GaP (green)</td>
<td>i</td>
<td>2.4 515</td>
<td>1 x 10⁻³</td>
<td>IX</td>
<td>~100</td>
</tr>
<tr>
<td>GaP (red)</td>
<td>d</td>
<td>2.4 515</td>
<td>1 x 10⁻³</td>
<td>IX</td>
<td>~100</td>
</tr>
<tr>
<td>GaP (green)</td>
<td>d</td>
<td>2.4 515</td>
<td>1 x 10⁻³</td>
<td>IX</td>
<td>~100</td>
</tr>
<tr>
<td>In₀.₂₂G₀.₇₈P (red)</td>
<td>i</td>
<td>2.1 590</td>
<td>3 x 10⁻⁴</td>
<td>VIII</td>
<td>330</td>
</tr>
<tr>
<td>In₀.₂₂G₀.₇₈P (green)</td>
<td>i</td>
<td>2.4 515</td>
<td>1 x 10⁻³</td>
<td>IX</td>
<td>~100</td>
</tr>
</tbody>
</table>

II. Ref. [88].
V. Ref. [89].
VI. Ref. [90].
VII. Refs. [65] and [52].
IX. Ref. [77]; please note that in this case a power efficiency of 10⁻⁴ is used to compute luminous efficiency.
Fig. 2. The band structure of the III-V compound semiconductors GaP (left; indirect band gap $X_5$-$I_3$) and GaAs (right; direct band gap $I_7$-$I_8$). In the case of GaAs, the electrons in the conduction band recombine with the holes in the valence band to generate a photon, and momentum is automatically conserved. In GaP, the electrons recombine with the holes to generate a photon through a phonon-assisted transition so that the crystal momentum can be conserved. The energy difference $\Delta_{so}$ is the spin-orbit splitting in the valence band.

GaP, some simple examples are: (a) recombination of an electron trapped on a donor, and a hole trapped on an acceptor, (b) a trapped electron at a deep donor recombining with a free hole, (c) excitonic (an electron and hole pair bound together as a pair) recombination at "iso-electronic" and other neutral traps. An iso-electronic trap refers to a bound state produced by an iso-electronic substituent (e.g. N replacing P in GaP). These iso-electronic traps, which are electrically neutral, could either be a point defect or a molecule in the GaP lattice. Such a trap can capture an exciton resulting in efficient radiative recombination. The best example of a point defect is a nitrogen iso-electronic centre which replaces phosphorus in GaP (green diodes). A well-known molecule-type iso-electronic trap is the Zn$_{Ga}^-$-O$_{P}^+$ nearest-neighbour complex which is responsible for the visible-red emission in GaP. Such iso-electronic traps provide the greatest impurity-induced luminescence efficiencies at room temperature in GaP, and will be discussed in detail in sections IV and V respectively. In section VI we shall discuss the problems associated with the formation of the neutral nearest-neighbour complexes.

In addition to the radiative recombination at these desirable impurity centres, it is very instructive to study competing nonradiative recombination mechanisms, which dissipate the injected electron energy and hence reduce the light output. For instance, at 4 K, the efficiency of the donor-acceptor transition in GaP is close to 100%. That is, for each injected electron, we obtain close to one photon out on the average. However, at room temperature (300 K) the quantum efficiency is less than 0.01%. This drastic decrease in efficiency is related to the fact that trapped electrons and holes have an appreciable probability of being thermally released from acceptors and donors at higher temperatures combined with the relatively low transition probabilities of D-A-pairs. Once back in the conduction band, they may find other nonradiative paths for recombination. Most of the energy released in exciton recombination at a neutral donor or acceptor goes into non-radiative processes. However, since the excitons at these centres are only very weakly bound, they are not expected to behave as nonradiative centres at high temperatures where thermalization is important. We shall postpone the important discussion of these nonradiative centres until section VII.

III. Donor-acceptor-pair emission

As mentioned earlier, the recombination mechanism involving simple donors and acceptors can be very efficient at low temperatures. Though they do not produce efficient light emission at room temperature, the understanding of the radiative recombination at these donors and acceptors has provided a great deal of information about the chemical nature of the donors and acceptors. We shall now discuss these recombination processes in more detail.

III-A. Shallow donor-acceptor-pair emission

Fig. 3 shows a photoluminescence spectrum taken at 1.6 K for S- and C-doped GaP. The emission is in the green region of the spectrum. The spectrum consists of a large number of sharp lines that culminate in a broad peak on the low-energy side. The understanding of the existence of all these lines from a simple system was provided by J. J. Hopfield, et al. As depicted in fig. 4, free electrons can be captured by positively charged (ionized) donors. Similarly, free holes can be captured by negative (ionized) acceptors. And, since the temperature is low, the electrons and holes will
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Fig. 3. Photoluminescence spectrum (intensity vs. photon energy \( h\nu \)) from nominally pure GaP at 1.6 K, depicting the donor-acceptor-pair spectrum. An electron bound to a sulphur donor recombines radiatively with a hole bound to a carbon acceptor. Different discrete separations between donor and acceptor lead to different lines. The numbers refer to the lattice shell number and are simply related to actual separations. The lines Rb are rubidium lamp-calibration lines; the line C arises from an exciton bound to a neutral sulphur donor; the lines A and B are due to a bound excitonic transition at the nitrogen isoelectronic trap. (From D. G. Thomas [81.)

stay put because there is not enough thermal energy to ionize them into the conduction or valence bands. However, this is only partially true, since electrons and holes have wave functions that spread out in the crystals away from the impurity atoms. Consequently, even though the donors and acceptors are separated from one another, there is a non-negligible overlap of wave functions which results in a finite probability of recombination of the electron and hole with the generation of a photon of visible light (see fig. 4). The emitted energy is equal to the band-gap energy minus the acceptor and donor binding energies plus a Coulomb term which, in its simplest form, is \( e^2/4\pi\epsilon r \):

\[
E(r) = E_g - (E_A + E_D) + e^2/4\pi\epsilon r. \tag{1}
\]

Here \( E_g \) is the forbidden-gap energy; \( E_A \) and \( E_D \) are the acceptor and donor binding energies; \( \epsilon \) is the dielectric constant and \( r \) is the actual separation between acceptor and donor. This Coulomb term can be considered as a correction to the donor ionization energy since the electron is not removed to infinity.

A most important aspect of the above equation is that since the acceptors and donors occupy discrete lattice sites, the observed spectrum consists of many sharp lines corresponding to discrete various values of \( r \). Thus, each line in the spectrum corresponds to recombination at donor-acceptor pairs with a particular separation. The intensities of these “pair” lines would be proportional to the number of pairs that can exist with a particular separation. Assuming that the donors and the acceptors are arranged randomly, the number of possible pairs does not increase regularly as the separation increases. The pattern of “pair” lines then can be used in establishing the shell numbers around the impurity, since one can obtain the exact value of \( r \) for a particular line. Once the value of \( r \) is known, one can plot the observed energy against the inter-impurity separator \( r \) and extrapolate to \( r = \infty \), obtaining from eq. (1) \( E_g - (E_A + E_D) \). Since \( E_g \) is known, if either \( E_A \) or \( E_D \) is known, the other can be accurately determined. This technique of obtaining \( E_A \) and \( E_D \) has been the most powerful way of determining binding energies. Another piece of information which can be
obtained from the intensity pattern and the plot of energy against \( r \) is whether the impurities (donors and acceptors) are on different lattice sites or on identical lattice sites. This additional information, besides giving the arrangement of the impurities on particular lattice sites, gives the specific atoms they replace (e.g. Ga or P). The binding energies for various impurities so obtained are listed in Table V of the reference of note [14].

Thus, the analysis of the pair spectra, combined with knowledge of the incorporated impurities, gives details of the physics of the radiative recombination mechanism as well as the chemical nature of the donors and acceptors.

Since at 300 K most of the zinc acceptors are ionized, we expect that any infrared emission due to the O-Zn donor-acceptor pair should be absent. There are however a considerable number of free holes approximately equal to the number of substitutional zinc atoms, in the valence band at these temperatures, which have a wave function like a plane wave and, hence, can interact with the deep bound electrons at oxygen donors. This interaction results in a bound electron to a free hole recombination process [23]. The detailed analysis of how the spectrum changes in going from a donor-acceptor recombination to a bound-free recombination, is depicted in fig. 6. The peak emission at 1.35, as the

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III-B. Deep-donor oxygen

Whereas the green luminescence due to shallow donor and acceptor pair emission is 100\% efficient at 1.6 K, it quenches as we approach room temperature since the carriers ionize and recombine through non-radiative “killer” centres. However, if the donor or acceptor is a deep trap, the pair luminescence may persist with reasonably good efficiency at room temperature. An example of this type of luminescence is that which is due to the deep-donor oxygen. The oxygen level is approximately 0.90 eV below the conduction band at 1.6 K. At room temperature the donor energy \( (E_D)_0 \approx 0.83 \text{ eV} \), which is approximately 32 \( kT \) at \( T = 300 \text{ K} \). Consequently, the electron trapped at the oxygen donors has a very low probability of thermalizing at 300 K.

The deeply trapped electron at an oxygen donor can recombine with a hole at an acceptor at low temperature. The pair spectra with Zn as the acceptor are depicted in fig. 5 [221]. The pair emission occurs in the near infrared region. From the analysis of O-Zn donor-acceptor-pair spectrum \( (E_D)_0 = 0.895 \pm 1 \text{ meV} \) was derived [221].

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Fig. 5. Infrared luminescence spectrum in (Zn,O)-doped GaP at 1.6 K due to pair emission involving the deep oxygen donor and the shallow Zn acceptor. The bracketed integers are the shell numbers and other numbers denote the pair degeneracy, accounting for the inequivalent pair sites within a given shell. The inset shows the isotope shift when some of the O\(^{16}\) are replaced by O\(^{18}\). (From P. J. Dean, C. H. Henry and C. J. Frosh [221].)

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Fig. 6. Temperature variations of spectral characteristics of the infrared luminescence spectra in (Zn,O)-doped GaP, depicting the shift from donor-acceptor-pair emission to bound-electron to free-hole emission. The two arrows on the top of the peak signify a shift of peak opposite to that of the band gap when the temperature decreases from 160 K (dots; peak at a) to 77 K (triangles; peak at b) suggesting the change in the nature of the optical transition.
temperature is raised, shifts to the higher energy. This can be simply explained by expressing the peak emission for the donor-acceptor \((DA)\) and bound-electron to free-hole \((BF)\) transitions as

\[
E_{na}^{DA} = E_A - (E_A + E_D) + \varepsilon_f^\text{er} - E_{\text{phonon}} \tag{2}
\]

and

\[
E_{na}^{BF} = E_A - E_D - E_{\text{phonon}}, \tag{3}
\]

where \(E_{na}^{DA}\) and \(E_{na}^{BF}\) are the observed peak energies of the donor-acceptor and bound-to-free transitions; \(E_{\text{phonon}}\) represents the energy of the contributing phonons which is the same in both cases, and is due to the tightly bound electron at the deep donor. In the O-Zn system \(E_A = 64 \text{ meV}\) and \(\varepsilon_f^\text{er} \approx 40 \text{ meV}\), which suggests that \(E_{na}^{BF}\) should be shifted approximately 24 meV towards higher energy. The observed shift in fig. 6 has a similar value. Thus, as the temperature is raised from 77 K, the transition has changed from dominant donor-acceptor to dominant bound-to-free. This is also consistent with the lifetime measurements performed on the deeply trapped electron as explained below.

In a simplified picture the decay time of the luminescence due to the radiative recombination of an electron with a hole follows a simple exponential law, i.e. \(I(t) = I(0) \exp(-t/\tau_D)\), where \(I(t)\) is the intensity of the luminescence at a given time \(t\) and \(\tau_D\) is the decay time. When \(t = \tau_D\), \(I(t)/I(0) = 1/e\). Hence the measured value of \(\tau_D\) is referred to as the \(1/e\) value. In the case of donor-acceptor spectra, the recombination kinetics are dependent on the lattice spacing so that decay rates are different for different sites. The observed decay rate is thus a sum of many exponentials, giving rise to a nonexponential decay; for convenience however it is described by a \(\tau_D\) of the \(1/e\) variety. In the case of recombination of the bound electrons with holes, the time decay should follow a true exponential law. Thus, by examining the time decay of the luminescence, one can determine whether the recombination is due to a donor-acceptor pair or due to a bound-to-free transition. This information was also used to confirm that above 150 K the infrared emission at 1.35 eV is due to a bound-electron/free-hole transition \([28]\).

Even though the infrared emission at room temperature is due to a deep electron recombining with a free hole, it is still not very efficient. This can be qualitatively explained by understanding the capture process for the conduction-band electrons into the ground state of the oxygen donor and is also due to the low concentration of these donors. Since the oxygen donor is deep, if an electron from the conduction band has to be captured into it, it has to lose energy equivalent to 17 optical phonons; the energy of one optical phonon is approximately 24 meV. This suggests that the probability of electron capture into this deep trap is extremely small. However, the electron can be captured into an excited state of the donor and then be transferred to its ground state through radiative energy transfer. In fact, this has been observed for oxygen by P. J. Dean and C. H. Henry \([34]\), and shown in fig. 7. The transition is referred to as an internal-capture luminescence in the oxygen donor. The lifetime of this internal-capture luminescence is measured to be approximately 20 \(\mu\text{s}\) \([13]\) at low temperatures. If we assume that this capture time remains constant with increasing temperature, one anticipates the oxygen donors to readily saturate as a function of increased injection of electrons in the conduction band. In the regime of saturation the effective capture time would be at least 20 \(\mu\text{s}\). If this is so, one could make an estimate of the quantum efficiency of the infrared emission by making a comparison with the quantum efficiency of the red zinc-oxygen complex emission. A capture time for the zinc-oxygen complex is approximately 20 ns.

We can conclude by comparison of the two capture times that the infrared emission should be approximately \(10^3\) times weaker than the red emission, which puts the infrared quantum efficiencies in the order of \(10^{-4}\). A further reason for the low infrared efficiencies is the low number of substitutional oxygen donors. Recent photo-capacitance data due to H. Kukimoto et al. \([26]\) suggests that the number of isolated oxygen donors in \(P\)-type GaP is approximately \(2 \times 10^{16} \text{ cm}^{-3}\). Though the oxygen donor does not play a major role as a radiative centre, we shall see later that it has produced very interesting radiative and nonradiative centres in association with either impurities or crystal defects (vacancies). Consequently, the chemistry of the incorporation of the oxygen donor becomes quite important towards the understanding of the formation of radiative centres.

IV. Isoelectronic traps; nitrogen

The discussion in the last section described the luminescence properties of an oxygen donor, which is a deep trap for electrons in GaP. In this section we shall discuss luminescence due to another class of impurities which exhibit some properties of a deep trap without actually possessing a large binding energy and are referred to as "isoelectronic" traps. These isoelectronic traps were discovered in GaP in 1965 \([36]\) and are crucial since they are capable of enhancing the recombination rate in an indirect-gap semiconductor. We shall discuss, mainly, why isoelectronic traps can generate efficient luminescence. The discussion will be related to nitrogen-doped GaP; nitrogen gives the simplest iso-
An isoelectronic \textit{trap} is an isoelectronic substituent (impurity atoms which are in the same column of the periodic table as the host atom replaced) which introduces a \textit{bound} state for either an electron or a hole. Once one carrier is bound, the centre is charged and the carrier of opposite sign is readily trapped through Coulomb attraction to form a bound exciton. For example, nitrogen occupies phosphorus sites in GaP and produces a bound state for electrons. Qualitatively, this can be understood since one expects nitrogen to be more attractive to electrons than is phosphorus, because of the more exposed nuclear charge of nitrogen. Thus, the electron is somewhat localized at the central nitrogen atom and hole attracted into a coulombic orbit. There is therefore a resemblance to an acceptor and the state is referred to as an “isoelectronic” acceptor \cite{28}. A heavier-element isoelectronic with phosphorus might be expected to produce a centre attractive to holes; an electron would then be bound by coulombic attraction and an isoelectronic donor would result. This is the situation when bismuth replaces phosphorus. Arsenic, on the other hand, does not produce a bound state in the forbidden gap of GaP \cite{13}.

Whenever a particle becomes bound to an impurity centre, it becomes localized in real space. Since real \( r \) and momentum space \( k \) are conjugate quantities, the wave function of the trapped electron is then much more extended in \( k \)-space. This is schematically illustrated as a large effect for the electron in fig. 8. The extent to which the wave function spreads out depends critically on the type of binding. In case of a normal donor or acceptor where the binding is coulombic, the wave function spreads out very little \cite{13}, as depicted for the hole in fig. 8. The reason is that this is a long-range force and produces no abrupt changes in the wave function in real space. However, there are short-range forces which are not coulombic in origin. This is the case of N in GaP, where the bound state for an electron is believed to occur primarily from the large difference in electronegativity between the N atom and the P it replaces. The bare pseudo-potential difference suggests that the binding energy of an electron should be of the order of 1 eV. Hydrostatic deformation of the GaP lattice around the bare N atom will tend to reduce this binding energy. The result is that nitrogen will bind an electron with about 10 meV of energy \cite{28-30}. The binding effect is felt only over one or two lattice spacings. Because of the highly localized distortions produced in that part of the electron wave function which is close to nitrogen atom, the electron wave function will extend throughout the \( k \)-space. Furthermore, due to the presence of a subsidiary minimum of
Fig. 8. A representation of the wave-vector ($k$) dependence of the probability densities (shaded area) of an electron bound to an isoelectronic trap (N in GaP) near the conduction band (energy at lower edge $E_c$) and of a hole bound to a shallow acceptor near the valence band ($E_v$ at top). The spread of the wave function of the electron in the $k$-space shown, is responsible for the efficient luminescence in N-doped GaP. (From D. G. Thomas.)

One interesting fact to note is that the deeper bismuth isoelectronic trap, to which the hole is bound by 0.04 eV, does not produce efficient luminescence at 300 K. This is because the transition probability is much lower for excitons bound to bismuth than for those bound to nitrogen. This is due to the fact that it is the hole which is bound by short-range forces and is spread out in the Brillouin zone. The band structure of GaP has no maximum in the valence band at the point corresponding to the conduction-band minimum. However, at this point, the valence-band edge is several volts removed from the $k = 0$ (zone centre) valence-band maximum. As a result, there is much less opportunity for direct electron and hole recombination for bismuth than nitrogen traps. One should also note that for neither isoelectronic trap do the phonon wings emphasize the momentum-conserving phonons that are often thought to be the mechanism by which optical transitions acquire strength in indirect semiconductors.

V. Nearest-neighbour complexes

The generation of red light in (Zn,O)-doped GaP uses both of the required properties for the efficient generation of light, i.e. (a) the trap should be deep so that no or little thermalization of the bound particles occurs, and (b) the localization of the electron and hole occurs through formation of the bound exciton at an "isoelectronic" trap. How this is brought about is very interesting. As we have seen in section III, the oxygen donor is approximately 0.83 eV deep at 300 K, and generates useless emission in the near infrared. It is deep, not because of coulombic attraction, but because of the same type of short-range forces which produce the attraction with nitrogen, i.e. a large proportion of
the bound-electron wave function is in the vicinity of the central cell. Consequently there is again a favourable spread of the electron wave function in $k$-space. To bring the binding energy into a useful range (from infrared to visible), it may be reduced by introducing a nearby acceptor with an opposite charge. In fact, this is what we find when the Zn atom is substituted on a nearest-neighbour Ga site. The negatively charged core of the Zn$_{Ga}$ acceptor reduces the binding energy of the electron to 0.24 eV and generates an isoelectronic trap (complex) which is a molecule $^{31}$ $^{32}$. This originally neutral Zn$_{Ga}$-O$_2^+$ centre, after having captured an electron, will bind a hole in a coulombic orbit. The recombination of electron and hole results in a trap (complex) which is a molecule $^{31}$ $^{32}$.

When chemically similar Cd was used in place of Zn, an entirely new spectrum was obtained, see fig. 10a. The spectrum consisted of a sharp A line at 1.907 eV at 20 K and more fine structure (phonon replicas) was observed as compared to the spectrum containing (Zn,O)-doped GaP shown in fig. 10b. The sharp non-phonon line allows one to perform precise experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig10a.png}
\caption{Luminescence spectra from (Cd,O)- and (Zn,O)-doped GaP, due to bound excitonic and pair-like transitions from Cd-O and Zn-O nearest-neighbour complexes. a) The time-resolved spectra due to the Cd-O complex. At time $t = 0$, the structured luminescence due to the exciton recombination at Cd-O complex dominates. This emission consists of a no-phonon line $A$ as well as local and lattice phonon-assisted transitions. At $t = 80$ ps a completely new spectrum appears which corresponds to a recombination of an electron at Cd-O complex with a hole at the Cd acceptor. b) The red spectrum in (Zn,O)-doped GaP at two temperatures. Though no fine structure can be seen, Zn-O emission possesses identical properties to Cd-O emission. The slit width is shown at the top left-hand corner of the figure. (See J. D. Cuthbert, C. H. Henry and P. J. Dean $^{38}$.)}
\end{figure}
From these experiments, which are described below, it has been shown that the red emission in (Cd,O)-doped GaP is due to a recombination of a bound exciton at a nearest-neighbour Cd$_{\text{Ga}}$–O$_{\text{P}}^+$ complex.

1. An extremely powerful way of identifying the chemical impurities responsible for the emission is to perform an “isotope” experiment in which an isotope of the element in question differing from the natural isotope is added. When isotope O$_{\text{18}}$ was added instead of normal O$_{\text{16}}$ isotope, the sharp A line shifted by 0.7 meV to higher energies [31]. Similarly, when isotope Cd$_{\text{114}}$ was added for Cd$_{\text{119}}$, the sharp A line did not shift significantly, but its phonon replicas did [32]. Without answering the difficult question as to precisely why these isotope shifts occurred, involvement of Cd and O was proven beyond doubt.

2. The relative orientation of Cd and O atoms could be determined from magneto-optical experiments [33]. At 1.6 K the hole and electron trapped at the centre freeze out from an energy level which corresponds to the A line in which the hole and electron spins are antiparallel, to an energy level 2.3 meV lower in energy in which the hole and electron spins are parallel. The transition corresponding to the lower energy is referred to as the B line. The Zeeman splitting of the B line is highly anisotropic. The data so obtained is consistent with a model in which Cd and O atoms are aligned along [111] directions, of which there are four in the crystal. If the magnetic field is along the [100] direction, all four become equivalent and only a simple pattern is observed. Since Ga and P atoms fall along [100] directions in GaP lattice, it is safe to say that Cd occupies a Ga site and O occupies an adjacent P site. The discrete-pair lines described in section III involving isolated O donors and Zn or Cd acceptors confirm the interpretation.

3. The nature of the recombination mechanism producing the emission could be verified further by studying the decay time of the luminescence. As discussed earlier, if the luminescence is due to a bound excitonic transition only, the decay is exponential. In case of Cd-O spectra, the decay was found to be nonexponential [39]. Furthermore, when time-resolved spectroscopy was performed (i.e., taking the spectra at different times after the exciting pulse had been switched off), one obtained two distinct spectra as shown in fig. 10a. This led to the interpretation that the deep bound electron at the Cd-O donor level can recombine radiatively either with a hole bound at the Cd-O complex or with a hole at the isolated Cd acceptors. (Schematically this is depicted for the Zn-O system in fig. 7.) Though the latter emission involved separated Cd acceptors, the emission is still different from the conventional donor-acceptor-pair spectra. The reason is that the Cd-O donor is neutral after recombination, and hence there is no Coulomb term in the equation for the energy of the emitted photon in eq. (1). This is also confirmed through time-resolved spectroscopy. Since in the bound excitonic transition the hole is localized, this emission should be dominant over the pair-like luminescence at room temperature.

4. Since the emission is due to a nearest-neighbour complex, thermal treatments can readily associate or dissociate the complex. The molecular bond between Cd and O or Zn and O in the GaP lattice can be broken around 900 °C and hence a fast thermal quenching from this temperature should decrease the red emission considerably. Conversely thermal treatments several hours long at lower temperatures (600 °C) should increase the number of complexes. In the case of Zn-O this has been confirmed [40]. We have used it to study extensively the kinetics of recombination leading to the red emission [41]. This type of study has enabled us to determine the relative strengths of the various competitive processes (both radiative and nonradiative). By definition a fully nonradiative process cannot be studied optically. However, the combination of thermal treatments with the recombination kinetic studies has in recent years yielded substantial information about them. We shall discuss this in some detail in the next section.

Just above we have discussed in detail the experiments performed on the Cd-O system. However, analogous properties are observed for the useful visible-red-emitting Zn-O complex, except for the sharp structure which is absent. In fact, the initial confusion in interpreting the red emission in (Zn,O)-doped GaP as due to conventional donor-acceptor-pair spectra, was due to two unexpected features of the spectra: firstly no sharp structure was seen, and secondly the pair-like spectrum coexists with the bound excitonic spectrum at a Zn-O complex.

**V-B. Kinetics of (Zn,O)-doped GaP**

The kinetics of radiative recombination of excitons bound to the nearest-neighbour Zn-O complex has been extensively studied in recent years [41-44]. We shall review some of the salient features of these studies and describe the principal results one obtains from it.

In the simplest model [41], recombination of electrons (the minority carriers) with holes (the majority carriers) in P-type (Zn,O)-doped GaP is depicted in fig. 11. The excited electrons in the conduction band can either be trapped at the Zn-O complex or disappear through other undesirable paths (henceforth referred to as nonradiative paths). The capture times into the Zn-O complex and thermal emission time out of the complex are given by $\tau_{\text{nt}}$ and $\tau_{\text{th}}$, respectively. The capture time...
Fig. 11. Schematic representation of recombination of minority electrons in P-type GaP(Zn,O) at 300 K. The capture time into the Zn-O complex is given by $\tau_{n}$; the thermal emission time out of the complex is given by $\tau_{nT}$. The capture time of non-radiative centres is represented by $\tau_{n}$. The decay time of an electron out of the complex and into the valence band is given by $\tau_{R}$ for radiative processes and $\tau_{NR}$ for nonradiative processes. $\tau_{n0}$ and $\tau_{0}$ represent the capture time into and decay time of an electron from the oxygen donor O, respectively.

for nonradiative centres is represented by $\tau_{n}$. The capture time for a particular impurity is inversely proportional to its concentration. The decay time of an electron out of the complex and into the valence band is given by $\tau_{R}$ for radiative processes and $\tau_{NR}$ for nonradiative processes. The measured decay time $\tau_{D}$ of the excitonic emission depends on the number of Zn-O complexes and the number of nonradiative centres through thermalization of the electron bound to a Zn-O trap ($E_{trap} \approx 0.24$ eV at 300 K) and can be expressed as:

$$\frac{1}{\tau_{D}} = \frac{1}{\tau_{R}} + \frac{1}{\tau_{NR}} + \frac{1}{\tau_{n}(1 + \tau_{n}/\tau_{nT})}. \tag{4}$$

The capture rates $1/\tau_{nT}$ and $1/\tau_{n}$ are respectively proportional to the number of radiative and nonradiative centres. The ratio of the concentrations of these two centres controls the quantum efficiency $\eta$, which is expressed as:

$$\eta = \left(\frac{\tau_{D}}{\tau_{R}}\right) \left(\frac{\tau_{n}/\tau_{nT}}{1 + \tau_{n}/\tau_{nT}}\right), \tag{5}$$

where $\tau_{R}$ and $\tau_{NR}$ depend on the free-hole concentration $p$. By plotting $\frac{1}{\tau_{D}}$ and $\eta$ as a function of $p$, one can estimate the value of $\tau_{n}/\tau_{nT}$ as given in fig. 12 and fig. 13. Two types of experiments have been done to get information on the ratio $\tau_{n}/\tau_{nT}$.

1. Crystals have been examined before and after the thermal treatments defined earlier, i.e. quenching and annealing. On annealing at 600 °C, one of the things that happen is that more Zn-O complexes are formed, resulting in an increased $\tau_{n}/\tau_{nT}$ ratio. The increased value of $\tau_{n}/\tau_{nT}$ results in higher efficiency and longer decay time as shown in figs. 12 and 13. On fast thermal quenching from $\approx 900$ °C, $\tau_{n}/\tau_{nT}$ decreases, which corresponds to lower quantum efficiency and a low value of decay time. Thus precise values of the parameter $\tau_{n}/\tau_{nT}$ can be obtained.

2. If other foreign impurities are added resulting in degradation of the lifetime, one can conclude that a particular impurity has changed $\tau_{n}/\tau_{nT}$, provided that $\tau_{R}$ and $\tau_{NR}$ remain constant, i.e. free-hole concentration does not change. Such an experiment has been performed with chlorine dopants and has been shown that it does in fact degrade efficiency and gives a lower decay time [48] as shown in figs. 12 and 13. A further discussion of nonradiative centres will be taken up in detail in section VII.

From the preceding data on decay time and efficiency, only $\tau_{n}/\tau_{nT}$ can be obtained. Several efforts [46] have been made in measuring the total minority-carrier lifetime $\tau_{L}$ which is defined through the equation:

$$\frac{1}{\tau_{L}} = \frac{1}{\tau_{n}} + \frac{1}{\tau_{nT}}. \tag{6}$$

When the thermalization time $\tau_{nT}$ is much shorter than the electron-hole recombination time $(1/\tau_{R} + 1/\tau_{NR})$,

Fig. 12. The decay time $\tau_{D}$ as a function of free-hole concentration $p$ in (Zn,O)-doped GaP measured at 300 K. Predicted values of $\tau_{D}$ are given by the solid lines using a value of the thermalization time $\tau_{nT} = 161$ ns and various values of the parameter $\tau_{n}/\tau_{nT}$. (See J. S. Jayson, R. N. Bhargava and R. W. Dixon [43].) Heat treatment of a sample with gallium chloride brings down the value of $\tau_{n}/\tau_{nT}$ suggesting that nonradiative contribution in the sample has increased [48]. The crosses refer to a sample annealed at 600 °C, the circles to a sample quenched from 1000 °C.
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Fig. 13. The quantum efficiency \( \eta \) of the conduction band electrons as a function of free-hole concentration \( p \) measured at 300 K. Predicted values of quantum efficiency are given by solid lines using a value of the thermalization time \( \tau_{th} = 161 \, \text{ns} \) and for different values of \( \tau_{n}/\tau_{th} \). (See Jayson, Bhargava and Dixon \[41\].) Heat treatment of a sample with gallium chloride brings down the value of \( \tau_{n}/\tau_{th} \) suggesting that the nonradiative path in the sample has increased. The squares represent the predicted internal efficiencies, the crosses and circles the measured external efficiencies for samples whose heat treatment took place with gallium chloride absent (crosses) or present (circles).

VI. The gallium-vacancy/oxygen complex

It has been known for some time that the commercially viable vapour-growth process did not produce efficient luminescence in GaP. Recent spectroscopic studies\[48-51\] on the vapour-grown material have yielded some valuable information about this fact and have further answered the question of how these radiative nearest-neighbour complexes like Cd-O \[52\] and the presence of certain nonradiative centres have been explained \[48\] \[53\].

VI-A. Identification

The discovery involved was the identification of a spectrum due to a bound excitonic transition at a nearest-neighbour complex of a gallium vacancy (\( \text{V}_{\text{Ga}} \)) and a deep oxygen donor at the adjacent phosphorus site \[49\] \[50\] (henceforth this complex is referred to as \( \text{V}_{\text{Ga}}-\text{O}_{\text{p}} \)). The spectrum from this complex occurs in the orange region and consists of a sharp no-phonon line at 2.117 eV at 1.6 K, designated as the line \( A \) in fig. 14. Additional structure is attributed to the lattice phonons and some weak vibrational modes. The intensity of the spectrum quenches rapidly with increasing temperature. The observed intensity of this characteristic orange luminescence (henceforth referred to as COL) is reasonably weak. The measured luminescent decay time for this emission is 110 \( \mu \text{s} \) at 4 K. The steps, which led to the identification of this COL luminescence as a bound excitonic transition at a \( \text{V}_{\text{Ga}}-\text{O}_{\text{p}} \) complex, are described below. The experiments were carried out on a water-vapour-grown GaP crystal which showed the strongest characteristic orange luminescence.

1. Annealing such a crystal at 400 °C for 15 hours in vacuum quenches the COL completely as shown in fig. 15a.

2. Indirect evidence for the existence of a \( \text{V}_{\text{Ga}}-\text{O}_{\text{p}} \) complex was obtained recently by Dean \[48\] in his study of the spectrum due to a complex \( \text{Li}_{\text{int}}-\text{Li}_{\text{Ga}}-\text{O}_{\text{p}} \); \( \text{Li}_{\text{int}} \) is the lithium atom at an interstitial location in the lattice. When Li was diffused in these crystals at 400 °C for 15 hours, emission due to \( \text{Li}_{\text{int}}-\text{Li}_{\text{Ga}}-\text{O}_{\text{p}} \) was observed. In this case the COL is completely quenched as

the decay time \( \tau_{D} \) equals \( \tau_{n} \). This occurs at reasonably high temperatures (\( \approx 500 \, ^\circ \text{C} \)). Under these conditions, \( \tau_{n} \) has been measured recently \[47\]. (Such a direct measurement of \( \tau_{n} \) yields the number of nonradiative centres which otherwise are too difficult to obtain through luminescence studies.)

It is clear that higher efficiencies could be achieved by either increasing the number of Zn-O complexes (radiative centres) or decreasing the number of nonradiative centres. In the next section we shall discuss how these nearest-neighbour Zn-O complexes are formed and how one can maximize their number.
predicted by Dean's model \[48\] of Li replacing a V\textsubscript{Ga} in a V\textsubscript{Ga}-O\textsubscript{P} complex. However, Li diffusion in already annealed crystals, in which the COL was completely quenched, gave at least 30 times less red luminescence due to Li\textsuperscript{int}-Li\textsubscript{Ga}-O\textsubscript{P}. This was strong evidence that the COL is associated with the V\textsubscript{Ga}-O\textsubscript{P} complex.

3. Strongest confirmation on the role of oxygen was again provided by the isotope experiments \[50\] where O\textsuperscript{18} was used in place of O\textsuperscript{16}. The data in the insert of fig. 14 shows the isotope shift which gives irrefutable evidence that oxygen is positively involved in centres giving rise to the COL.

4. Magneto-optical data suggests \[50\] that the transition is due to a bound exciton and that the final state is a neutral double acceptor. In the neutral acceptor the spins of the two holes are paired off. Furthermore, it is determined that the tight binding of the exciton (by 160 meV) to V\textsubscript{Ga}-O\textsubscript{P} contains an appreciable contribution from the bound hole, unlike the Cd-O or Li\textsuperscript{int}-Li\textsubscript{Ga}-O\textsubscript{P} complex, where the hole is weakly bound to the electron by a long-range coulombic attraction.

**VI-B. Role of the V\textsubscript{Ga}-O\textsubscript{P} complex**

Having confirmed that COL is due to an electronic transition at a V\textsubscript{Ga}-O\textsubscript{P} complex, we discuss below some of the aspects of the existence of such a complex which we believe to be important in the formation of some of the radiative and non-radiative complexes in GaP.

1. The elements of the Group II column of the periodic table such as Cd, Zn, Mg, and Be can fill the gallium vacancy of the V\textsubscript{Ga}-O\textsubscript{P} and produce nearest-neighbour radiative complexes (e.g. Zn\textsubscript{Ga}-O\textsubscript{P}). This mechanism of formation is believed to occur because of the following reasoning. The charged state of the V\textsubscript{Ga}-O\textsubscript{P} is a double acceptor, i.e. (V\textsubscript{Ga}-O\textsubscript{P})\textsuperscript{--}, as determined by the magneto-optical data on the sharp A line in COL \[50\]. The Zn atom is assumed to diffuse in GaP by an interstitial-substitutional mechanism. Furthermore an interstitial Zn atom is positively charged, i.e. donor-like. The coulombic attraction between Zn\textsuperscript{int}+ and (V\textsubscript{Ga}-O\textsubscript{P})\textsuperscript{--} can thus lead to the formation of a neutral complex Zn\textsubscript{Ga}-O\textsubscript{P}; this process is described by the equation:

$$Zn\textsuperscript{int}+ + (V\textsubscript{Ga}-O\textsubscript{P})\textsuperscript{--} \rightarrow Zn\textsubscript{Ga}-O\textsubscript{P} + e.$$  (7)

Thus the V\textsubscript{Ga}-O\textsubscript{P} complexes play the crucial role of precursors to the formation of radiative Zn\textsubscript{Ga}-O\textsubscript{P} complexes, and it becomes necessary to control and optimize the concentration of V\textsubscript{Ga}-O\textsubscript{P} complexes in order to have a control over the Zn\textsubscript{Ga}-O\textsubscript{P} complex concentration \[51\] \[54\]. This will be discussed later in section VI-C.

2. Another important aspect of the V\textsubscript{Ga}-O\textsubscript{P} complexes is their behaviour in Zn-doped water-vapour-grown crystals. The spectra before and after annealing are shown in fig. 15b. After annealing, strong quenching of COL occurs with simultaneous increase in the red Zn-O complex emission at 1.86 eV, indicating an increase in the number of radiative centres. However, the intensity of the green Zn-S donor-acceptor-pair spectrum also increases, suggesting that the V\textsubscript{Ga}-O\textsubscript{P} complex may be acting as nonradiative centres at low temperature.

3. Lastly, the quenching of the COL on annealing at temperatures of \(\approx 400-500^\circ\text{C}\) can be attributed to the formation of centres like C\textsubscript{Ga}-O\textsubscript{P} or Si\textsubscript{Ga}-O\textsubscript{P} which act as nonradiative centres \[45\] \[53\]. How these centres act as nonradiative centres is discussed in section VII. However, the formation in these centres is guided by an equation (say for Si), similar to eq. (7):

$$Si\textsuperscript{int}+ + (V\textsubscript{Ga}-O\textsubscript{P})\textsuperscript{--} \rightarrow Si\textsubscript{Ga}-O\textsubscript{P} + 3e.$$  (8)
Thus in all GaP crystals, both radiative centres like ZnGa-Op and nonradiative centres like SiGa+-Op+ are formed during the annealing process. Understanding the equilibrium constant for the formation of these various complexes from the V_ga-op complex is therefore necessary to optimize the quantum efficiency of the material. Considerable work is in progress and we shall briefly discuss some of the important results obtained to date in section VI-C.

An important discovery which has resulted from the study of V_{Ga-O_p} complexes is that the element Mg can be incorporated in place of the gallium vacancy in the V_{Ga-O_p} complex, giving rise to new efficient yellow-orange emission, attributable to a bound excitonic transition at a nearest-neighbour Mg-O complex [52][55]. The details of the optical properties of this emission are discussed in section VII.

VI-C. Formation of V_{Ga-O_p} complexes

The maximization of the number of V_{Ga-O_p} complexes is rather important for the formation of more Zn-O radiative complexes, as expressed in equation (7) in the last section. Since the characteristic orange luminescence is attributed to the bound excitonic transition at a V_{Ga-O_p} complex, its relative intensity should give the relative number of V_{Ga-O_p} complexes. We describe briefly the experiments which have been performed recently on water-vapour-grown GaP crystals [51] to maximize the number of V_{Ga-O_p} complexes, utilizing the spectral studies on COL.

Several pieces of the same water-vapour-grown GaP crystals were annealed at different temperatures ranging from -500 °C to 1000 °C and subsequently quenched. Annealing time varied from 2 hours at lower temperatures to 15 minutes at higher temperatures. The resultant photoluminescent intensity of the COL obtained in these crystals is plotted as a function of the quenching temperature in fig. 16. The data goes through a sharp maximum with activation energies of 3.3 eV and 1.25 eV respectively on the high- and low-temperature sides of the curve. It is interesting to note that the emission intensity decreases sharply on both sides of the maximum for two entirely different reasons: the low-temperature region is consistent with an impurity incorporation as given by eq. (8), and the decrease at high temperatures represents the dissociation of the gallium-vacancy/oxygen-donor complex. Understanding of both of these processes is rather crucial for the maximization of the quantum efficiency in (Zn,O)-doped GaP since one produces more nonradiative centres and the other destroys the associated complexes responsible for generating radiative centres. These concepts are being put into practice presently to increase the quantum efficiency in (Zn,O)-doped GaP.

VII. Mg-O nearest-neighbour complexes

Since an Mg acceptor is smaller in size and less electronegative than Zn, one anticipates that the bound exciton emission from a Mg_{Ga-O_p} complex would be shifted towards a higher energy than that from a Zn_{Ga-O_p} complex [52][55]. Recently an efficient emission in the yellow-orange region (peak at 6030 Å at 300 K) has been observed in (Mg,O)-doped GaP [52][55]. This emission is attributed to a bound excitonic emission at a nearest-neighbour complex [52]. Confirmation of the role of oxygen is again obtained from an O^{18}-isotope experiment [55].

This yellow-orange luminescence in Mg-diffused samples, at low temperatures, is shown in fig. 17a. The luminescence consists of two separate bands: a structured luminescence designated as spectrum A, and a structureless spectrum designated as spectrum B. Time-decay experiments (fig. 17c) and luminescence-excitation experiments have been used to derive the energy-level diagram in fig. 17b, and the two different spectra A and B are attributed to the radiative recombination of electrons at an Mg-O complex with either a hole at the Mg-O excitonic level E_o to produce the exciton spectrum A, or a hole at an isolated Mg acceptor level E_A to produce the pair spectrum B. This is similar to the dual "exciton" and "pair" spectra discussed in section V for Cd-O and Zn-O complexes. The ratio of Mg-O, A and B spectra depend critically on the ratio \((\text{Mg-O})/(\text{Mg})\). However, as expected, the room-temperature emission is mainly due to the exciton transition.

It is important to note that on thermal quenching from 950 °C, the Mg-O complexes can be destroyed
with simultaneous appearance of the COL originating at the $V_{Ga-O}$ complex. This strongly suggests that formation of Mg-O is preceded by the formation of a $V_{Ga-O}$ complex. As noted earlier, optimization of the $V_{Ga-O}$ complexes is therefore an important step in the improvement of the efficiency of GaP light-emitting diodes which utilize isoelectronic nearest-neighbour complexes as radiative centres.

The external quantum efficiency of photoluminescence in (Mg,O)-doped GaP has been measured to be greater than 50% at 100 K. Diodes have been fabricated by growing a Te-doped N layer on solution-grown platelets. An external quantum efficiency of $\approx 0.1\%$ has been measured at 77 K. Optimization of the room-temperature quantum efficiencies requires a further increase of Mg-O complexes near the junction and/or a significant reduction in the nonradiative centres which, in addition to the normal capture process, capture electrons that thermalize from the relatively shallow (Mg-O)-complex level.

VIII. Nonradiative centres

Nonradiative recombination mechanisms — those that release energy as heat (e.g. lattice vibrations) but do not produce light — are difficult to study since direct observation of this process is almost impossible. However, they play a very important role in the light emitting properties of indirect semiconductors. The quantum efficiency in GaP at room temperature is indeed limited by electron-hole recombination at these non-radiative centres, as discussed in section V-B. Consequently, a discussion of the nature of these centres is important, since their concentration must be reduced in order to achieve significantly higher quantum efficiencies in LEDs.

The most relevant nonradiative process in these semiconductors is the Auger process. In the Auger process, energy released due to electron-hole recombination, instead of being carried away by a photon, is transferred as kinetic energy to a nearby third particle (electron or hole). This third particle could be bound or free. Several cases have been studied and we discuss here three of these relevant cases which are separately depicted in fig. 18.

The first case relates to S-doped GaP in which S acts as a shallow donor. At low temperatures neutral sulphur can bind an exciton giving rise to an excitonic transition at 2.309 eV at 4.2 K commonly referred to as the C-line \cite{57}. The measured lifetime of the C-line luminescence is 21 ns. The radiative lifetime estimated from absorption and electrical measurements for the above transition is $\approx 11\ \mu s$. This amounts to a discrepancy of a factor 500 between observed and the estimated values for the lifetime. This discrepancy can be explained if the state not only decays radiatively, producing the C-line luminescence, but also decays nonradiatively by an Auger process. In this Auger process, the bound electron at the sulphur atom takes the energy released in the exciton annihilation (fig. 18a), this nonradiative
process being 500 times more rapid than the radiative decay.

It is known that all neutral acceptors \[^{58}\] \[^{59}\] and donors \[^{60}\] bind excitons at low temperatures and that the resulting emission is primarily nonradiative. However, these centres do not act as nonradiative centres at room temperature, because the excitons are already dissociated at this temperature.

The second type of Auger process is related to neutral centres such as the Zn-O complex (fig. 18b). In efficient \(P\)-type (Zn,O)-doped material, free holes are in abundance at room temperature \((\approx 5 \times 10^{17} \text{ cm}^{-3})\). Whenever the bound hole of the exciton recombines with the deep bound electron, energy could be transferred as kinetic energy to one of the free holes, resulting in an Auger process \[^{61}\] \[^{62}\]. To get a large number of Zn-O complexes, the concentration of Zn doping is required to be high \[^{63}\]. However, at these high concentrations, the nonradiative process due to Auger recombination dominates \[^{41}\] \[^{42}\]. Hence, an optimum Zn concentration has been found. For the best diodes \[^{18}\] it amounts to approximately \(3 \times 10^{17} \text{ cm}^{-3}\).

An alternative approach to achieve higher efficiencies is to achieve a large number of Zn-O complexes, without doping with a large number of Zn atoms. Experiments in this direction are in progress \[^{51}\].

One point concerning the two types of isoelectronic traps (i.e. N and Zn-O complex) is worth making. As we have seen, high concentrations of Zn result in predominantly nonradiative Auger processes. It is however fortunate that isoelectronic traps like N by definition do not add charge carriers to the crystals and hence do not promote nonradiative Auger recombinations — e.g. no impurity-band Auger effects \[^{64}\]. The most efficient green diodes, in fact, contain a nitrogen doping greater than \(10^{19} \text{ cm}^{-3}\) and yellow nitrogen-doped GaP diodes contain approximately \(10^{18} \text{ cm}^{-3}\) N atoms \[^{65}\].

Lastly, we discuss a group of nonradiative centres which are deep centres and could act as nonradiative centres at room temperature. These centres are doubly ionized centres, which are capable of binding two particles of the same type. Let us take for an example the case of Cl doping in GaP. Since Cl is a Group VII element it will replace P to generate deep doubly-ionized donors \[^{45}\] \[^{66}\]. Normally, Cl\(^{++}\) atoms can capture two electrons. If there are free holes available, hole and electron recombination will take place. However, this energy does not result in photon generation, but instead can be transferred to the second bound electron at the chlorine atom (fig. 18c). Similarly, when inadvertent impurities like Si or C fill the V\(_{Ga}\) of the V\(_{Ga}\)-O\(_{P}\) complex, doubly ionized complexes like Si\(_{Ga}^{+}\)-O\(_{P}^{+}\) and C\(_{Ga}^{+}\)-O\(_{P}^{+}\) result. These centres are again doubly charged and will promote strong Auger recombination \[^{53}\] \[^{67}\]. Certain properties of these doubly ionized centres are summarized below.

(a) Since these centres are doubly ionized, the capture cross-section of such centres is expected to be large \[^{67}\], i.e. they can control the recombination kinetics in GaP. (b) Impurities like Cl and Si are inadvertently present in most GaP crystals, and in fact may be major factors currently limiting the observed quantum efficiency. Their removal should result in higher observed quantum efficiencies, both in diodes and in bulk crystals.

An interesting comment on the various types of growth processes used for making GaP diodes should be made here. Recently, diodes have been made by vapour-phase epitaxy \[^{68}\] and liquid-phase epitaxy \[^{69}\] in which green luminescence is attributed to the radiative recombination of the free exciton and its phonon-assisted transitions. In these diodes it seems that the low quantum efficiencies as well as the luminescence decay time are limited by the presence of the nonradiative centres. In both types of diodes a luminescence decay time of 400 ns has been observed, which possibly suggests that the concentration of nonradiative impurities in vapour-phase and liquid-phase epitaxially grown GaP is approximately the same.

IX. Concluding remarks and future developments

As can be seen from the preceding discussion of radiative centres, the recent improvements in quantum efficiency and range of colour give a promising future
to GaP LEDs. However, one question remains to be answered: "What is the theoretical upper limit on the external quantum efficiency in this indirect semiconductor?" Stated in practical terms, "Can we ever hope to produce a solid-state lamp capable of generating lumens of optical power?"

Thus far no theoretical predictions have been made based on the physics of the radiative recombination at localized centres in GaP. Because of the importance of this question, we shall attempt a semiquantitative answer [70] in the case of radiative recombination at the Zn-O complex, which is the primary centre discussed in this article.

To achieve the higher quantum efficiencies in (Zn,O)-doped GaP, one requires that the ratio of the radiative centres (in this case the number of Zn-O complexes) to nonradiative centres be as high as possible. The reduction of the nonradiative centres is achieved (a) by reducing Zn concentration to avoid Auger processes due to free holes on the P-side, and (b) by reducing nonradiative impurities like C+-O+ or Si+-O+, etc.

Presently, the number of Zn-O complexes, $N_{\text{Zn-O}}$, achieved is approximately $3 \times 10^{16}$ cm$^{-3}$ for the Zn concentration, $N_{\text{Zn}}$, to be $3 \times 10^{17}$ cm$^{-3}$, i.e. $N_{\text{Zn-O}}/N_{\text{Zn}} = 0.1$. By understanding the thermodynamics of the formation of these complexes, one can hope to achieve $N_{\text{Zn-O}}/N_{\text{Zn}} \approx 1.0$. Initial calculations in this direction [71] suggest that to maximize $N_{\text{Zn-O}}/N_{\text{Zn}}$, one should incorporate Zn after the number of $V_{\text{Ga}}$-$O_{\text{P}}$ complexes has been maximized. Furthermore, nonradiative centres like Si+-O+ or Cl++ can be avoided by growing crystals without these unwanted impurities. Alternatively, impurities like Si+-O+ can be minimized by appropriate heat treatment [56].

Assume that one can obtain $N_{\text{Zn-O}}/N_{\text{Zn}} = 1.0$ and a considerable reduction in the nonradiative impurities by appropriate growth conditions and thermal treatments. Then, in our model as discussed in section V-B, this would correspond to $\tau_R/\tau_{\text{int}} \gg 1$, and from the estimated variation of $\tau_D$, $\tau_I$ and $\tau_{\text{NR}}$ as a function of free-hole concentration (fig. 12), we predict $\tau_R \approx 3000$ ns and $\tau_D \approx 1500$ ns for $N_{\text{Zn}} \sim 10^{17}$ cm$^{-3}$. From these numbers eq. (5) gives $\eta \approx 50\%$. Such a high value of quantum efficiency may be possible in the near future.

Using quantum efficiencies of 50% in red diodes, one can think of large-area indicator light sources as one of the possibilities for solid-state lighting. A comparison is made with an incandescent lamp of 15 W which generates approximately 10% of its power in the visible and 1% in the red (i.e. 1.5 W of visible-light output and 0.15 W of red-light output). The luminous efficiency of such a lamp is about 10 lm/W corresponding to about 1 lm/W in the red region of the visible spectrum. A red diode of quantum efficiency 50% at 2 V d.c. and 50 mA would generate 0.05 W of optical power in the red. An array of three diodes would correspond to 0.15 W of optical power which is the same as generated by the incandescent lamp in the red region mentioned above. Furthermore, the luminous efficiency of these red diodes would correspond to 10 lm/W because of the higher quantum efficiency.

In the case of the radiative centres responsible for green and yellow emission in GaP, much more research is required before similar projections can be made. However, because of the greatly increased sensitivity of the eye in these regions, efficiencies of 1 to 10% would already give 5-50 lm/W.

It has been suggested recently that the high efficiencies in nitrogen and (Zn,O)-doped GaP might lead to stimulated emission of coherent radiation, i.e. laser action and experiments aimed at this goal have been reported [72] [73]. However, a characteristic inhomogeneous broadening is observed [73] instead of the expected line narrowing and further work is needed to clarify whether laser action in the visible is occurring in GaP. Beside GaP and the III-V ternaries, there are some other semiconductors which could be potential candidates for the future study of radiative centres.

An example is SiC, which can give blue light; injection luminescence can be produced in both N- and P-type as well as several polytypes. The two most interesting forms are the cubic (β-SiC) and rhombohedral (α-6H), which possess indirect energy-band gaps of 2.38 eV and 3.08 eV at 0 K respectively. Since the melting point of SiC is $\approx 2600$ °C, this semiconductor has been plagued by a serious growth problem. Furthermore the physics and the chemistry of these nonradiative recombination centres in SiC has not been studied in that great detail, primarily because no proper controlled doping of material has been done. Epitaxial layers have been grown to achieve yellow or blue diodes with relatively poor efficiency at desirable injection level [74] (Table I).

GaN, on the other hand has a band gap of 3.50 V and is a direct band-gap semiconductor. High photoluminescent efficiencies (12% at 300 K) [75] and laser action by optical pumping [75] have been recently achieved in this semiconductor. The fundamental problem with GaN besides availability of a single-crystal growth process is that only N-type GaN has been produced to date. Making it P-type may not be feasible as noticed in the case of other direct wide-band semiconductors like the II-VIs. To date, GaN diodes of the insulating-to-N-type have been made by Zn diffusion exhibiting green and blue d.c. electroluminescence at room temperature [77]. The external power efficiency is $10^{-4}$ and an external quantum efficiency of $10^{-2}$ has been achieved.
A review of progress on the radiative and nonradiative centres in GaP has been presented, which clearly demonstrates that mutually beneficial interaction can be derived between the physics of the subject on the one hand and the chemical aspects of the subject on the other. How far the LEDs will advance towards true commercial viability processes. At present it seems that these solid-state lamps will enjoy a bright future.

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Bibliography


Recently a qualitative estimate was made (J. M. Dishman, Int. Electron Devices Meeting 1970, Washington, D.C., p. 154, Abs. 24.2), which suggests that removal of nonradiative centres by a factor of 10 can only increase of a factor of 2 in the quantum efficiency of diodes. However, such calculations are based on several estimated parameters (concentration of radiative centres, capture cross-sections, etc.) and would change the results as these parameters are determined more accurately.

G. M. Blom, unpublished work.
Microwave electronics

Recent years have seen so many changes taking place in microwave technology that the whole field is taking on a completely new look. The greatest changes are to be seen, naturally enough, in the laboratory, but the impact on the manufacturers and the user is already considerable. In the past microwave technology was concerned with relatively large and expensive components such as magnetrons, klystrons and waveguides. Today, however, lower-power microwave signals can be generated and processed in solid-state elements, and these are small and much less expensive. With these new components systems can now be made that earlier would have been inconceivable, and microwave equipment is no longer excluded from some likely applications because it is too large or too expensive. At last even the non-professional applications have become a practical possibility.

This issue of Philips Technical Review includes twelve articles that describe microwave studies at various Philips laboratories and give an impression of the nature of these new developments. They are introduced by an article that gives a general account of present trends and also includes a look at the likely pattern of future developments.