SPECTROSCOPIE DE DÉFAUTS - LUMINESCENCE
THE ANALYSIS OF WIDE BAND GAP
SEMICONDUCTORS BY OPTICAL
SPECTROSCOPY

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THE ANALYSIS OF WIDE BAND GAP SEMICONDUCTORS
BY OPTICAL SPECTROSCOPY

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Résumé. — A la suite d'une brève récapitulation des nombreuses techniques optiques significatives et de leurs avantages pour l'analyse des impuretés, le texte principal met l'accent sur la spectroscopie d'absorption et de luminescence. L'auteur examine les conditions requises pour la meilleure exploitation possible de la méthode. L'analyse à basse température utilisant les cristaux semiconducteurs assez bien purifiés nécessite beaucoup de dispositifs électroniques modernes. L'analyse courante peut être rapide et non destructrice et particulièrement appropriée à la détection et la reconnaissance (luminescence) ou à l'évaluation quantitative (absorption) de certains types d'impuretés, souvent celles qui sont les plus intéressantes dans les dispositifs électriques et optiques. Des exemples sont donnés, surtout pour GaP et GaAs, des nombreuses techniques possibles pour relier les caractéristiques importantes des spectres optiques aux différents types d'impuretés donneurs, accepteurs et pièges isoelectroniques, et de leur extension à l'identification d'espèces chimiques.

Abstract. — Following a brief summary of the wide variety of relevant optical techniques and their advantages in impurity analysis, the main text emphasizes absorption and luminescence spectroscopy. Attention is given to the conditions required for greatest exploitation of the method, analysis at low temperatures using the relatively refined semiconducting crystals needed in many current electronic devices. Routine analyses can be swift and non-destructive, particularly suited to the detection and recognition (luminescence) or the quantitative estimation (absorption) of certain types of impurity, often just the ones of greatest general interest in electrical and optical devices. Examples are given, mainly in GaP and GaAs, of the variety of techniques available to link key features in the optical spectra with the different classes of impurity, donors, acceptors and isoelectronic traps, and their extension to the identification of chemical species.

1. Introduction. — Most semiconductor devices depend for their operation on the presence of the right impurities in correct positions in the crystal lattice. For convenience we can define the related impurity or defect-dominated properties as extrinsic. A variety of analytical techniques exist to determine the composition of solids, including atomic absorption and emission spectroscopy, mass spectroscopy, X-ray fluorescence, proton back scattering and activation analysis. Surfaces can be characterized by several specific techniques. These can typically provide sensitivities

\[ \sim 1 \text{ ppm a, or } 4-5 \times 10^{16} \text{ atoms in } 1 \text{ cm}^3 \]

of a typical solid. Several of the techniques become very difficult when we seek the ubiquitous elements B, C, O, Mg, Al, Si, S, Fe and Cu. Unfortunately, these elements are most likely to dominate the properties of refined material, they include many of the persistent, inadvertently present impurities. We are concerned here with a very important commercial field. Semiconductors and the devices made from them represent a world market currently estimated at \( \sim 20 \text{ billion per annum} \).

The demands on analysis depend very much on the device. In semiconductors, light emitting diodes (LEDs) are formed from pn junctions with quite heavy doping to provide the desired high bulk conductivity, certainly in the \( 10^{17} \text{ cm}^{-3} \) range and often \( \geq 10^{18} \text{ cm}^{-3} \), especially for the direct gap variety. One might then think that an analytical sensitivity of \( \sim 1 \text{ ppm a} \) is quite sufficient. However, the operation of these devices, particularly the indirect gap variety, depends upon the control of the impurity-induced recombination of minority carriers injected through the pn junction. For an efficient device, the carriers must recombine in a particular manner, through transitions at the advertently present recombination centre, the luminescence activator. Unfortunately, the available concentration of suitable centres is often quite low, particularly for centres with deep levels which produce light at energies well below the semiconductor band gap \( E_g \). Red GaP : Zn, O lamps provide a good example; the maximum available concentration of the ZnGa2O4 luminescence activator is \( \sim 10^{16} \text{ cm}^{-3} \) [1]. Thus we need sensitivities of \( \leq 0.2 \text{ ppm a} \) for the analytical control of such LEDs. Solid state microwave sources operating at 10 GHz require n-type material with carrier concentrations in the low \( 10^{15} \text{ cm}^{-3} \) range, which can only be provided by advertent doping in the materials used, for example GaAs. The electron mobility must
be high, so the compensation level should be low. Impurity control in solid state microwave amplifiers is still more stringent at a given operating frequency. As far as we know, the presence of shallow compensating acceptors as well as deep trapping levels of any type is entirely deleterious to the operation of these devices. We therefore need very good quality semiconductor material, whose properties must be defined through analysis at sensitivities $\lesssim 0.02$ ppm ($\sim 10^{14}$ cm$^{-3}$).

It is natural to seek analysis of semiconductor material using the properties basic to the operation of the device itself. Right from the beginning, semiconductors were analysed through electrical measurements. As is well known, combination of measurements of the Hall effect and conductivity provides the concentration and mobility of the majority carriers. At an appropriate temperature, the concentration is essentially $N_D-N_A$ in an n-type crystal and the mobility can be measured at a temperature where it is dominated by ionized impurity scattering.

Conveniently, 300 K is sufficient for nearly complete ionization of the relevant shallow donors, $E_D \lesssim 0.1$ eV while the compensation level can be estimated from the impurity-limited mobility measured at 77 K. Use of the Brooks-Herring analysis of carrier scattering at ionized impurities in the derivation of the total concentration of ionized impurities from measurements of carrier mobility at 77 K have been discussed by Wolfe, Stillman and Dimmock [2] for n-type GaAs. While this information is very important, it is limited and the technique has the following disadvantages.

a) It is relatively slow, requiring special specimen preparation. Thus, good quality contacts have to be prepared and the desired material properties may be influenced in subtle, often unrecognised ways by the necessary contact preparation treatments. The micro Hg probe represents a considerable advance here for certain semiconductors, particularly since solid state pressure contacts may well irreversibly damage the semiconductor surface. These electrical transport properties of epitaxial layers can only be measured on substrates of relatively high resistivity, an inappropriate form for most devices. Schottky barrier capacitance can provide the profile of $N_D-N_A$ in an epitaxial layer on a conducting substrate, but it is an even slower analytical technique, usually requiring the deposition of a special Au surface layer.

b) As usually performed, electrical measurements provide no evidence of the identity of the donors or the compensating acceptors. As is well known, such information can be obtained from a study of electrical transport throughout a wider temperature range containing the onset of thermal ionization of the majority donors. These analyses are extremely tedious, to such an extent that they are not usually performed on a routine basis. The results can be difficult to interpret, because the effective donor or acceptor ionization energy is significantly dependent on the total (donor and acceptor) impurity concentration in the usual concentration range of device relevance. Often, many subtle effects must be considered before impurities can be recognised reliably from activation energies derived from the temperature-dependence of electrical transport properties. Thus, Neumark [3] in a recent analysis of impurity activation energies for the shallow Zn acceptor in GaP notes that the effect of screening by impurity ions as well as by free carriers must be considered. The screening results in a reduction with increase in temperature of the effective activation energy obtained from Hall data, needed to account for the experimental results on GaP: Zn. The activation energy is reduced by 50 % when the screening parameter

$$a_0 | N_D-N_A |^{1/3} \sim 0.1 \rightarrow 0.2,$$

where $a_0$ is the radius of the unperturbed acceptor. This occurs for $| N_D-N_A |$ in the low $10^{14}$ cm$^{-3}$ range, where we shall see that certain types of optical spectra (particularly d-a pair spectra [4]) remain only weakly perturbed, providing impurity identification and estimates of $E_A$ still free from significant corrections associated with the impurity concentration. It is impossible to recognise in the electrical transport data the simultaneous presence of two donors whose ionization energies do not differ by more than, say 25 % at equal concentrations. Recognition of the presence of a minor donor at concentrations say $\lesssim 10$ % of the major is very difficult unless their ionization energies differ widely. Even the hard won data taken over a wide temperature range provide no information on the nature of the compensating acceptors, since there is no dependence on $E_A$.

The advent of optoelectronic semiconductor devices, particularly LEDs naturally re-emphasises the possibility of material analyses using optical spectroscopy, the subject of this talk. We shall see that the optical techniques complement the traditional electrical ones. They are particularly suited to the detection and recognition of impurities. The simultaneous presence of several different donors and acceptors can be recognised in a single measurement. The characteristics of certain types of optical spectra, such as the d-a pair spectra already mentioned, which depend only on the low radius electronic ground states of the impurity centres, are less sensitive to the obscuring effects of interimpurity interactions than the results obtained from electrical analyses. The relative concentrations of impurities of a given type, which produce generically similar spectra, can be estimated readily from most types of optical spectra. Luminescence spectra, a main feature of this talk, provide only an order of magnitude indication or perhaps set a limiting value for the absolute concentration of the impurity centres. The absolute concentration can be estimated from a variety of types of optical absorp-
tion spectra, which often depend on the preparation of the impurity or defect centre in a prescribed electronic state. However, the optical absorption technique requires initial calibration in most cases, usually performed by comparison with the electrical data. Certain optical techniques can provide absolute concentration information, for example photocapacitance. However, this technique again requires preparation of some type of electrical contact. Photocapacitance is particularly useful for the characterisation of the deep centres which often limit the performance of semiconductor devices and which, for a variety of reasons, may not produce detectable luminescence or significant optical absorption. Such techniques lie outside the scope of this talk. My objective today is to provide a quick survey of the exploitation of optical spectroscopy, particularly luminescence, in the detection and recognition of some of the most obvious impurities in semiconductors. I will emphasise spectra connected with donors, acceptors and some neutral centres such as point defect isoelectronic traps and certain d-a associates.

2. Main text. — (Fig. 1) Summarises the classes of electronic spectra. I should say immediately that another optical technique exists, namely impurity phonon absorption spectroscopy. This technique can have sensitivity down to 1 ppm for certain important impurities, particularly those whose mass is significantly less than the host atom replaced or which are bound interstitially with large force constants. Like some of the electronic spectra discussed here, phonon spectroscopy can provide information not only on the concentration of these impurities (also requires calibration) but particularly on the lattice site and state of association of the impurity. However, it is worth noting here that in favourable cases equivalent information can be obtained from the structured sidebands which occur in the electronic spectra of impurities. An example of this will be provided later in the talk. Impurity phonon absorption spectroscopy has the particular advantage that the relationship between the energy of the impurity mode and the normal modes of the host lattice can be predicted with a considerable degree of confidence. However, many detailed effects remain obscure and the strength of the absorption depends upon a dynamic charge parameter which is not well correlated with the presence of static excess charge at the impurity and seems best determined by empirical means. This type of impurity phonon spectroscopy, involving wave-lengths \( \geq 5 \mu \) and frequently \( \geq 10 \mu \), has been reviewed elsewhere [5] and is outside the scope of this talk. We should simply note that only certain impurities can be detected in a sensitive manner from the phonon spectra, just as only certain types of impurity provide readily detected electronic spectra in semiconductors. It is useful that the selection (sensitivity) criteria are quite different, so that these two optical analytical techniques are often complementary. The electronic spectra often provide appreciably higher levels of concentration sensitivity because they are obtained in an energy range covered by much more sensitive optical detectors, the near infra-red, visible or ultraviolet, and are less subject to obscuring effects of absorption from intrinsic lattice vibrations or from electronic transitions due to weakly bound or free electronic particles. We can say that the electronic spectra provide considerable information about the vibrational states of the impurity and also of the host lattice, briefly illustrated later in the talk. The reverse is not usually true except in certain very special cases, for example the LO phonon bound at a neutral donor or acceptor [6].

(Fig. 2) Contains an energy level scheme for several donors and acceptors in GaP, and certain transitions between them and the valence and conduction bands.

**Fig. 1.** — A listing of types of electronic spectra in semiconductors.

**Fig. 2.** — Schematic optical transitions involving shallow and deep donors and acceptors. Important centres in GaP have been selected for illustration.
An intra-centre recombination is shown for the deep donor O. Bound exciton transitions do not appear, otherwise the major generic types of impurity-induced electronic transitions are shown. The ionization energies of the relevant impurity centres are often small, less than 200-300 meV. They act as carrier trapping rather than recombination centres at 300 K, a necessary consequence of the fact that many are deliberately added to provide controlled electrical conductivity in electronic devices which must operate at room temperature. Liquid nitrogen temperature spectra are usually adequate for the impurity phonon analysis technique already mentioned. However, we shall see that the techniques for recording optical spectra at He temperatures are trivial nowadays and should discourage no-one. High spectral resolution is essential to take full advantage of the technique.

(Fig. 3) Reviews the information which can be obtained from electronic spectra.

**DIVIDENDS FROM ELECTRONIC SPECTRA**

1. **Presence of many impurities revealed - high sensitivity and often specificity**
2. **Specificity - appearance of characteristic spectral energy, often \( e \) or \( n \) binding energy at impurity**
3. **Specificity - type of impurity through detailed properties of transition, sometimes even type of substitutional site eg in AB ZINCBLende material**
4. **Concentration of impurity, usually order of magnitude, sometimes with precision**

**Fig. 3.** Information provided by extrinsic electronic spectra in semiconductors.

(Fig. 4) Compares several optical techniques—need for contacts, sensitivity and ability to measure concentration. Sensitivity may well be much better than 1 ppma.

(Fig. 5) Shows the equations for cross-section in optical absorption. The term \( C \) is given by

\[
\frac{2\pi^2 e^2 \hbar}{m^* c} (E_{\text{eff}}/E)^2
\]

where \( (E_{\text{eff}}/E)^2 \) is the local field correction between the average macroscopic field of the photon \( E \) and the local field \( E_{\text{eff}} \) at the impurity central cell. It is \( \sim 1 \) for an extended state in a covalent centre, but may be much larger for a deep state. The Lorenz form, valid for extreme localisation is \( \frac{1}{9} (n^2 + 2)^2 \), which is \( \sim 20 \) for a typical III-V compound semi-

**BASIC EQUATIONS FOR CROSS-SECTIONS**

**Impurity electronic absorption per centre**

\[
\int \alpha dv = \frac{f f_{\text{ex}}}{n}, \quad n = \text{refractive index}
\]

\( f = \text{oscillator strength, } \sim \text{ for isolated intra-centre transition, often } \ll 1 \text{ for band-impurity transition, especially for indirect semiconductor} \)

\( f_{\text{ex}} \) defined/mol of semiconductor \( (0.0025 \text{ in CdS}) \)

\( n \) is number of mols covered by \( e-n \) overlap \( (\sim 1000 \text{ in CdS}) \)

\[ n = \text{number of mols covered by } e-n \text{ overlap} \]

\[ f_{\text{ex}} = \text{defined/mol of semiconductor} \]

\( \text{Detailed balance, relates lifetime } \tau \text{ and } f \)

\[ \tau = 4.5 \lambda^2 / n f, \quad \lambda \text{ is wavelength} \]

**Fig. 5.** The use of optical spectra for the determination of concentrations.

**TECHNIQUE AND QUANTITATIVE ASPECT**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Contacts</th>
<th>Sensitivity</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical absorption</td>
<td>NO</td>
<td>Variable, especially if not intra-centre</td>
<td>QT (needs calibration especially if not intra-centre)</td>
</tr>
<tr>
<td>Luminescence</td>
<td>NO</td>
<td>Variable, excellent in favourable cases</td>
<td>QL (approx from linewidths and kinetics)</td>
</tr>
<tr>
<td>Raman scattering</td>
<td>NO</td>
<td>Reasonable in special cases</td>
<td>QL/QT (absolute for bound phonon)</td>
</tr>
<tr>
<td>Photoconductivity/photocapacitance</td>
<td>YES</td>
<td>Generally reasonable</td>
<td>QT (absolute for photo-capacitance)</td>
</tr>
</tbody>
</table>

QT—Quantitative, QL—Qualitative

**Fig. 4.** A comparison of various optical analytical techniques.
conductor. With this form, the relation for the optical cross-section is known as the Smakula formula, widely used in the study of colour centres in ionic crystals [9]. Note the giant oscillator strength of Rashba and Gurgenishvili, specifically relevant for the absorption of weakly bound excitons [10]. The total oscillator strength of the absorption at an isolated centre, say a donor is calculable for a given form of interaction potential. For example:

$$f = \frac{16\pi^2 e^2 \hbar}{3\hbar^3 c} \left(\frac{h\nu - E_D}{E_D}\right)^{3/2}$$

for a deep donor where a δ-function potential may be used [11]. The features seen most easily in optical absorption are the transitions from the ground state to the bound excited states, which occur an energy slightly lower than required for optical ionization of the donor. Unfortunately, the fractional oscillator strength of these transitions is very low for very deep states, and the dominant delta function impurity-electron interaction may well exhibit no bound excited states. Another problem for a deep centre is that much of the oscillator strength may be contained in phonon sidebands, which are less likely to show well resolved, easily measured structure [12]. On the other hand, a shallow donor, whose states are well represented by a long range Coulomb potential shows relatively strong interbound state transitions and a relatively much weaker photoionization continuum. We show later the readily detected data typical for shallow donors in GaAs.

(Fig. 6) Shows the simple experimental equipment needed for photoluminescence or optical absorption. We have already noted that the samples must be mounted in a low temperature cryostat. For the study of luminescence from relatively inefficient activators, where strong optical pumping with a focussed laser beam is highly advantageous, as well as for measurements at the lowest temperatures, it is essential to immerse the sample directly in liquid refrigerant. If slightly higher temperatures, $\geq 6$-10 K and weaker optical pumping can be tolerated, then very simple and cheap means exist [13] whereby temperatures stable to $\pm 0.5$ K can be readily attained, granted a supply of liquid He.

(Fig. 7) In luminescence, particularly, the properties of the sample may be examined in detail across the surface (limited by beam focus, readily down to $\sim 100$ μ) and in depth (limited by the ambipolar carrier diffusion length $\sim 1$ μ). Profile information can be obtained from luminescence studies of suitably step-etched samples. Angle-lapping, often used for electrical profiles [14], is not very appropriate for photoluminescence analysis under strongly absorbed exciting light. Work damage often has a strongly deleterious effect on the intensity and spectral form (influence of strain [15]) of luminescence originating close to the semiconductor surface. Photoconductivity may be used as well. As we will see, this enhances the signal from transitions to relatively shallow excited states of the impurity, whereas thermalisation ensures the dominance of the deepest excited states in luminescence spectra.

(Fig. 8) Shows the optical absorption of thin, chemically polished layers of epitaxially grown GaAs [15A]. The intrinsic exciton absorption predominates. Traces of impurity absorption also occur, despite the small layer thickness (10 μ and 2 μ) and the low impurity concentration, $N_D - N_A \sim 10^{14}$ cm$^{-3}$. The theory of
Rashba and Gurgenishvili predicts $f \sim 10^6 f_{\text{EX}}$ for excitons bound to neutral donors in GaAs. This results in $f \sim 4$ and $\tau = 1.8$ ns for radiative recombination, close to the observed value [16].

(Fig. 9) Interband intrinsic electronic absorption is generally some $10^3$ weaker in an indirect gap semiconductor like GaP. Impurity-assisted absorption is also usually proportionately weaker. However, given an appropriate form of electron-impurity interaction, it is possible to obtain impurity-induced absorption with large oscillator strength. Thus, for the well known isoelectronic trap $N$ in GaP, the wave-function of the electron bound to this neutral centre contains a large admixture of components associated with the conduction band from the direct gap at the zone centre. The strong absorption is consistent with expectation for a shallow bound electron state in the central field of a $\delta$-function potential well [17]. The oscillator strength exceeds 0.1, and the $N$-induced absorption changes the room temperature body colour of thin slices of GaP from honey brown to red at modest impurity concentrations $\sim 10^{18}$ cm$^{-3}$. This is the basic reason why $N$ is such an effective activator for green luminescence in GaP. The greater absorption near the bandgap corresponds through detailed balance to a greatly enhanced probability for green band-edge luminescence. The $N$ concentration can be determined from low temperature optical absorption at the sharp bound exciton no-phonon line down to $< 10^{14}$ cm$^{-3}$ in a sample 1 mm thick. This concentration can be

![Graph of absorption edge](image)

**Fig. 9.** — A portion of the absorption edge of undoped GaP (intrinsic spectrum) and of GaP containing $7 \times 10^{18}$ cm$^{-3}$ isoelectronic $N_p$ (only $1.5 \times 10^{18}$ cm$^{-3}$ according to ref. [19]) (extrinsic spectrum).
measured absolutely from optical spectra using the oscillator strength determined from the lifetime observed for the allowed electronic transition, relating absorption and luminescence by detailed balance [18]. However, recent charged particle activation analyses for $N$ in GaP have provided a significant correction to the oscillator strength [19]. A much more dramatic discrepancy between separately measured values of $\tau$ and $f$ for donor bound excitons in GaP: $S$ and Si: As led to the recognition of the dominance of non-radiative (Auger) recombinations of excitons bound to centres containing additional weakly bound electronic particles [20] in indirect semiconductors.

(Fig. 10) We must have high quality crystals to exploit optical spectroscopy fully in the detection and measurement of impurities in semiconductors. We need sharp spectra for identification, but the non-phonon lines are very sensitive to the macroscopic state of the crystal. For example, inhomogeneous crystal requirements for detailed recognition

**Impurity Level Must Be Large Enough for Detection But Sufficiently Small to Avoid Strong Inter-Impurity Interactions and Plasma Screening (For Centres with Excess Charge Carriers)**

For free excitons, Hanamura shows that binding energy

$$E_x' = \frac{E_x}{1 + X} \quad N_D = \left( \frac{1 + X}{1 + X} - 1 \right) \frac{1}{12a_0^3}$$

where $a_0$ is the donor Bohr radius

For $E_x'/E_x = 0.9; N_D/N_H > 0.5$

$N_H$ defined for Hott insulator to metal transition

$N_H = 1/64 \sigma_0^3$

Stark broadening in addition for bound exciton on intra-impurity transitions

**Fig. 10.** The concentration broadening of optical no-phonon lines

strain broadens the spectral lines, and they split into clearly resolved subcomponents in the uniform strain fields often inadvertently present [15]. These effects are particularly noticeable in zincblende semiconductors, where they are dominated by splitting of the $F_S$ valence band. Typical deformation potentials which relate stress and strain are a few eV, and splittings of $\sim 10$ meV may occur for stresses $\sim 1$ kbar (10 kg, mm$^{-2}$). Indirect gap zincblende semiconductors contain extra effects due to the removal of the degeneracy of electron states derived from equivalent conduction band valleys under stresses of appropriate symmetry. This sensitivity of the optical spectra may be turned to advantage in enabling the inhomogeneity of the built-in strain to be probed across the surface of a semiconductor slice.

The spectra are also sensitive to free carrier screening of the interaction between the impurity and the electronic particle. The screening of free carriers is usually described in the Debye approximation, with the Debye screening radius $(\kappa T/4 \pi n_e^2 m^*)^{1/2}$. Bound states whose unperturbed radii are large compared with this radius cannot exist. We are concerned with shifts and broadenings of spectral lines at temperatures and concentrations where no free carriers occur, unlike the screening problem in electrical transport studies [3]. Hanamura has shown that the dominant effect on free or bound exciton lines is screening due to the dielectric effect of neutral donors, which predominate when $m_e^* < m_h^*$ and therefore $E_D < E_A$. Note that the screening criteria depend upon the cube of the Bohr radius. For a hydrogenic centre, this means that the sensitivity to such screening effects of the states of principal quantum number $n$ is proportional to $n^6$, a large effect! This is the reason that broadened but barely shifted optical no-phonon lines occur under doping conditions where electrical data show strong deviations from the dilute concentration limit. As already mentioned, electrical transport in p-type GaP: Zn gives $E_{\gamma} \sim 0.5 E_A^{0.9}$ near $N_A-N_D = 10^{18}$ cm$^{-3}$, when strongly broadened but essentially unshifted no-phonon lines from recombinations at d-a pairs of separation $\sim 20$ Å can still be recognised [3, 4].

Stark broadening also occurs due to interaction between a bound exciton, say and a nearby ionized impurity of either sign (the energy shift is proportional to $|Z|^{2}r^5$).

(Fig. 11) According to Hanamura [21], the Stark interaction lowers the bound state peak energy by an amount $4 \left( \frac{8}{7} \right) N_{Ea}^{4/3} \sigma_0^4 E_{cs}$ compared with the value given from screening alone and causes an asymmetric line profile with a low energy tail varying like $(\Delta E)^{-7/4}$. The effect has been analysed in n-type CdS and is strong in the high concentration region of metallic impurity conduction [22]. At the present, its contribution to the structured low energy wing often seen for bound excitons at intermediate impurity concentrations in GaP [23] is a matter of conjecture. Stark broadening of donor photoexcitation spectra in GaAs, illustrated later, has a genetically similar origin.

(Fig. 12) The recognition of impurities in optical spectra comes largely from their characteristically different transition energies. This is a particularly powerful method when the spectra show sharp lines so that differences between closely similar impurities of a given type can be recognised clearly. Not all electronic transitions give sharp no-phonon lines, as indicated.

(Fig. 13) Given the presence of sharp no-phonon lines, we can recognise the generic nature of the transition not only from the spectral form (transition energy, strength of phonon cooperation) but also from certain perturbation spectra. Most useful, I believe, are the perturbations (line splittings and shifts) produced in a
FIG. 11. — The luminescence of excitons at neutral Cl donors in CdS for various concentrations of neutral donors (from ref. [22]).

magnetic field. Again, we need no contacts to the sample, but unfortunately a rather large magnetic field. A line splitting of \( \sim 0.8 \text{ meV} \) or \( \sim 6.5 \text{ cm}^{-1} \) requires 35 kG at \( g = 2 \), a typical value. We analyse the magnetic effects in terms of the magnetic splittings of the upper and lower states between which the electronic transitions occur. I take the example of an exciton bound to a neutral donor in a wurtzite semiconductor, where:

\[ g_L = 2, \text{ and is isotropic, due to the electron} \]

\[ g_u = g_h \cos \theta, \text{ where } \theta \text{ is the angle between } c \text{ and } H, \]

due to the hole, assuming the two electrons are in an antisymmetric spin state.

The upper state is a Kramers doublet because the 4-fold valence band characteristic of the zincblende-semiconductor is split by the axial crystal field of the wurtzite lattice structure [24].

(Fig. 14) A simple but very revealing Zeeman spectrum results, illustrated for point defect N substitutional donors in 6 HSiC [25]. We see that the \( g_u = 0 \) when \( \theta = 90^\circ \), as predicted, and the spectrum is a simple doublet whose splitting gives \( g_u \) directly. The larger outer splitting \( |g_u + g_L| \) also disappears

**CHARACTERISTIC ENERGIES IN OPTICAL SPECTRA OF DIFFERENT TYPES OF IMPURITY**

<table>
<thead>
<tr>
<th>IMPURITY TYPE</th>
<th>TRANSITION</th>
<th>PHOTON ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>DONOR (D) OR ACCEPTOR (A)</td>
<td>INTERNAL (S)</td>
<td>( C.E_{D,A} ) WHERE ( C ) IS 3/4, 6/9, -- FOR HYDROGENIC CENTRE</td>
</tr>
<tr>
<td></td>
<td>FREE-TO-BOUND (B)</td>
<td>( E_g - E_{D,A} + kT )</td>
</tr>
<tr>
<td></td>
<td>D-A PAIR (S OR B)</td>
<td>( E_g = (E_A + E_D) + e^2/r_{DA} + f(r_{DA}) )</td>
</tr>
<tr>
<td></td>
<td>BOUND EXCITON (S)</td>
<td>( E_{gX} = C.E_{D,A} ) (C IS SOMETIMES ( \sim 0.1 ) - ‘HAYNES RULE’)</td>
</tr>
<tr>
<td>ISOELECTRONIC TRAP (I) (MORE GENERALLY, NEUTRAL TRAP)</td>
<td>I-D,A PAIR (MB)</td>
<td>( E_g = (E_I + E_{D,A}) + f(r_{1D,A}) )</td>
</tr>
<tr>
<td></td>
<td>BOUND EXCITON (S)</td>
<td>( E_g = (E_I + E_{D,A}) )</td>
</tr>
</tbody>
</table>

\( \text{\( E_I, \sim EM \) BINDING OF } e \text{ OR } h \text{ TO POINT CHARGE IF } E_I \text{ IS LARGE} \)

\( ^n \text{NO-PHONON LINES ARE SHARP(S), MODERATELY BROAD(MB) OR BROAD(B) AS INDICATED.} \)

FIG. 12. — Characteristic energies for various types of extrinsic electronic spectra in semiconductors, neglecting phonon interactions.
when $\theta = 0^\circ$, but for a different reason. The intensity of the corresponding transitions contains a term $[1 - |\cos \theta|^6]^2$ [24]. The splitting of the remaining doublet yields $|g_s - g_h|$. (Fig. 15) Similar effects can occur in a zincblende semiconductor. We consider an axial donor where the degeneracy of the valence band is lifted locally in the crystal field of the axial centre. My example is a Li-related donor in GaP. Now, there is a complication in that the donor has a $<111>$ type symmetry axis, but at a given crystal setting $H$ cannot lie along, or be perpendicular to each of the 4 sets of crystallographically equivalent $<111>$ directions. Although the Zeeman spectra are now more complex, analysis of the spectrum defines the symmetry axis in a way familiar in electron spin resonance spectroscopy. Again, the $g$-values of the electron and hole can be obtained very directly from these Zeeman spectra, here $g_s = 2.00$, $g_h = 0.89$ [26]. The Roth three-band theory [27] provides a fair estimate of the reduction in electron $g$-value below the free electron value of 2.0 in narrow direct gap semiconductors like GaAs [28] and InSb [27]. However, rather small changes in the absolute $g$-values typical between different centres in a given semiconductor have not received much theoretical exploitation. The extent to which a given set of $g$-values conforms to existing knowledge provides a powerful check on the validity of a given assignment for an impurity-related electronic transition and empirical trends have been noted which sharpen such fitting criteria [7], [29]. (Fig. 16) Amongst the relatively covalently bonded semiconductors, there has been a considerable amount of work on magnetic analysis of impurity bound exciton spectra in GaP. I show a collection of data for excitons bound to a variety of neutral centres; isoelectronic point defects or isoelectronic associates. Here, there is a simplification in that there is no free spin in the lower state, which contains no exciton so that $J = 0$, $g_s = 0$. However, $J$-$J$ coupling allows two or three upper (exciton) states for a point defect, split by the electron-hole exchange interaction. The splitting of the lower energy, $B$ or $J = 2$ exciton state in the cubic field for a $T_d$ impurity site may be negligible, as for the $N$ exciton [30], or readily detected, as for the Bi exciton [31]. Its presence contributes a large anisotropy to the magnetic splittings of line $B$ until the Zeeman splittings $\geq E_{Hi}/E_{B2}$, 0.28 meV for the Bi exciton. The magnetic splittings of an exciton bound to an axial, $C_{3v}$, isoelectronic trap are complex due to the type of orientational effect already noted for the Li donor exciton. Again, the symmetry axis can be readily defined from the magnetic data. The Li$\text{I}_{\text{Li}}$-Ga$_2$O$_3$ [32] centre has been chosen for the example rather than the centre of similar type studied earlier [33], $C_{3v}$-Ga$_2$O$_3$, because more of the theoretically predicted subcomponents were detected for the Li-related centre. Exciton binding to a centre of still lower symmetry,
possibly C$_2$, with a large crystal field splitting, causes the reappearance of a simple, isotropic Zeeman spectrum. There are at least two candidates for the C$_2$, symmetry Sb$_p$-Sb$_p$ associate in the luminescence of GaP : Sb, one shallow exciton near 2.326 eV with just the expected pair of states $J = 0$ and $J = 1$ and a much deeper bound exciton with no-phonon components near 2.29 eV, including a second unexpected pair splitting like $J = 0$ and $J = 1$ bound excitons [34]. Since then, a number of bound exciton doublets with similar magnetic properties have been seen in GaP [35] as well as excitons bound to neutral axial acceptors containing holes with quenched orbital angular momenta both in GaP[34] and GaAs : Cu [36]. In all these spectra, it seems important that the hole rather than the electron should interact strongly with the impurity; for example the $N$, ($N_p$-$N_s$) bound excitons [37] split more like a minor perturbation of the behaviour of an exciton bound to isolated $N_p$ than like the simple model for Sb$_p$-Sb$_p$ given in figure 16.

(Fig. 17) As a simple example of information available in the phonon sidebands of an electronic transition, I show the luminescence of $N$ in GaP [38]. The form of most of the structure down to the strong peak labelled A-LO is very similar to the one phonon density of states of the perfect GaP lattice. This distribution has been calculated using the lattice vibrational dispersion curves determined from inelastic neutron scattering [39]. When examined in detail, the broader replicas due to acoustical phonon-assisted transitions show many of the slope discontinuities known as van Hove singularities. At lower transition energies, a well defined peak appears, caused by an overtone of a symmetrical local mode vibration involving $N_p$. The fundamental is weak because of symmetry considerations. The energy of the local mode $W_{\text{loc}}$ is closely approximated by the simple expression

$$W_{\text{loc}} = k^{1/2} \left( \frac{1}{2M_G} - \frac{1}{M_N} \right)$$

where $k$ is a force constant, here essentially that of the Ga-P bond [37], the $M_s$ are the masses of a Ga and $N$ atom and $\sigma$ is a factor which is empirically $\approx 1.3 \rightarrow 2$ for a number of local modes in III-V semiconductors [5]. The presence and behaviour on isotopic substitution of this local mode provides the best possible evidence for association of the spectrum with $N_p$. Generally, as the localisation energy of the exciton increases, that is the centre becomes a deep trap, the proportional strength of the local mode effects increases. In addition, the general strength of the coupling to all types of phonon increases. For a more complex centre, say an axial defect, the fundamental local mode vibrations can also give strong spectral satellites. These effects are well documented in the exciton luminescence of the axial centre Li$_s$-Li$_s$-O$_p$ in GaP, where true local modes, gap modes and in-band resonance modes of Li and O all appear [32].

(Fig. 18) I believe a good case has been made for the role of optical spectroscopy in the quantitative estimation of impurities in semiconductors and for the recognition of particular impurities through analysis of the generic transitions they induce. I now turn to a brief survey of very recent work on the recognition of different donors and, particularly acceptors in GaAs through optical spectra. Personally, I have found it amazing that our studies and applications interests in GaAs have been carried as far as they have without anyone being able to identify convincingly the residual impurities which control the electrical properties of refined GaAs. This is particu-

![Fig. 17](image1.png)

**Fig. 17.** — The luminescence of excitons at the $N_p$ isoelectronic trap in GaP, showing the two no-phonon lines A and B resulting from $J-J$ coupling (Fig. 16) and the form of the phonon sideband including the local mode overtone replica A-2 LO, of energy 121.8 meV (from ref. [38]).

![Fig. 18](image2.png)

**Fig. 18.** — The energies of free to bound bands reported in the edge luminescence of relatively lightly doped GaAs, and the chemical assignments where given. The first two columns contain recent data reported in reference [42], obtained from RRE (vpe) and STL (lpe) GaAs. The remaining data was extracted from references [41a]-[41m]. $^4$ denotes an electrical measurement.
larly remarkable for the acceptors, where the chemical shifts are much larger than for the donors, as I shall show. I mentioned before that the concentrations of these acceptors are poorly controlled at a level where they give significant compensation in typical GaAs X-band microwave devices, a very uncomfortable situation. Of course, people have previously attempted to identify acceptors in GaAs, many using photoluminescence [40]. They correctly anticipated that the technique should work particularly well for acceptor recognition. Unfortunately, until recently there has been no concerted body of work capable of providing a definitive link between spectral effects and chemical species. Much of the earlier work was performed with material of inadequate purity. Some recent workers avoided this problem, but established the nature of their acceptor impurities by allegedly reasonable guesswork. I show that this produced a very confused literature, particularly for the more common acceptors C, Si, Zn. As you will guess, I believe we have now removed this confusion through the data shown in columns I and II of figure 18.

(Fig. 19) Shows the generic form of the acceptor and donor bound exciton spectra, as well as the free to bound and donor-acceptor pair spectra and the intrinsic exciton luminescence of a typical direct gap semiconductor such as GaAs. The whole effect is

![Diagram of spectral effects](image)

**Fig. 19.** A schematic representation of the low temperature edge luminescence of a refined, direct gap semiconductor such as GaAs. The two-electron replicas in the EX-N DONOR lines are displaced nearly 3/4 \( E_D \) below the parent lines for the hydrogenic shallow donors characteristic of GaAs, while the corresponding displacements for the acceptor (two-hole) satellites, 2h bear a more complex relationship with \( E_A \) [ref. [42] and [47]]. Here N means neutral, not nitrogen.

usually known as the edge luminescence, although some restrict this term to cover only the \( F \to B \) and D-A pair components, not mutually resolved in this representation. I will describe these latter spectra and the exciton spectra separately. Particularly note the satellite labelled 2h from the principal bound exciton doublet labelled EX-N acceptor. I will show that this satellite provides valuable confirmation for the existence of the divers acceptor species to be discussed [42].

(Fig. 20) Contains the characteristic temperature dependence of the \( F \to B \) and D-A pair spectra over the temperature range in which appreciable thermalisation of the shallow donors (\( E_D \sim 6 \text{ meV} \)) commences. The free to bound, \( F \to B \) transitions predominate at \( T \gtrsim 15 \text{ K} \) in GaAs, the exact temperature depending somewhat on the optical pumping rate. The spectra to be reported here were obtained using relatively low densities of photoexcitation. At this temperature, when \( kT \sim E_D/4 \), the majority of the electrons recombine from the bottom of the valence band rather than when trapped out on the shallow donors. I believe that in the absence of structure due to transitions at discrete D-A pairs, and short of using the more complicated technique of time-resolved spectroscopy, the \( E_X \) values are best obtained from analyses of the \( F \to B \) band. The positions and shapes of the \( F \to B \) bands are less subject to details of the observational technique. However, these bands are best studied at the lowest temperatures at which the D-A pair bands remain negligible, using dilutely doped samples. Both of these precautions are intended to minimise spectral broadening.

(Fig. 21) Summarises \( F \to B \) spectra from a series of judiciously acceptor doped GaAs, as well as showing typical spectra for undoped, refined vpe and lpe GaAs. From these data, the quite distinct set of dominant residual acceptors in the latter material can be determined with some confidence [42]. We find that vpe GaAs from a variety of laboratories contains Zn as the principal acceptor impurity, while lpe GaAs is usually
Fig. 21. A comparison of the edge luminescence of a set of refined GaAs lightly backdoped with the indicated acceptors, made at 15 K where the free-to-bound components are seen in near-isolation (Fig. 20). The vpe material always tends to show the Zn band, while undoped lpe GaAs shows bands due to C, Si and Ge (7). The relative strength of the C band shown here underestimates the relative concentration of C acceptors since this shallow luminescence band undergoes significant preferential thermal ionization at 15 K (from work leading to ref. [42]).

![Diagram of band structure](image)

Fig. 22. — The energies of the broad free-to-bound bands and «two-hole» satellites (to the left) of the exciton-neutral acceptor bound exciton components (right) in the edge photoluminescence of refined GaAs, lightly back-doped with the indicated shallow acceptors. The lower two rows illustrate spectra typical of undoped GaAs of state of the art purity (from work leading to ref. [42]).

![Diagram of energy levels](image)

Fig. 23. — Relationship between 1s and 2s binding energies of shallow acceptors in GaAs, including the theoretical datum T for a hydrogenic acceptor (ref. [47]). The relevant experimentally observed transitions are indicated in the inset, where BE and TH denote bound exciton and two-hole transitions. The transitions 1s → 2p appear in infrared photoexcitation (ref. [46]), (from ref. [42]).
and with effective mass variational calculations of Lipari and Baldereschi [47]. The relevant effective mass levels, their classification scheme and the bound exciton transitions we observe are illustrated. It is clear that the excited state responsible for the "two hole" satellites is 2S3/2, an even parity state. Knowledge of the 1S binding energies determined from the \( F \rightarrow B \) spectra enables us to calculate the binding energies of the 2S states. These lie on a smooth curve, interestingly independent of whether the acceptor is on the Ga or As lattice site. The curve extrapolates back to the theoretical (effective mass) point \( T \). The goodness of this agreement between the theoretical and experimental spectra makes it quite clear that the levels all arise at \( T \) symmetry, point defect acceptors.

(Fig. 24) In contrast to the valence band, the conduction band in GaAs is simple, non-degenerate and nearly spherical. The donor photoexcitation spectra have been studied in the far infra-red near 250 \( \mu \), using Fourier Transform spectroscopy. The levels follow a scheme very similar to the \( H \) atom. In particular, the \( p \) excited states split linearly in a magnetic field according to expectation for an orbital effect, \( \Delta E_{\text{m}} = eH/m^*c \) with \( m^* = 0.066 5 \) \( m_0 \) [48]. It is convenient to record photoconductivity spectra, where the two step photo-thermal ionization process ensures that structure due to transitions to high excited states becomes favoured if the temperature is suitably adjusted. As we noted earlier, peaks due to inter-bound state transitions are strong compared with the structure due to direct photo-ionization for a shallow Coulombically bound centre. These lines become narrower and the \( s \rightarrow p \) lines appreciably stronger as \( H \) increases.

(Fig. 25) It is convenient to examine the \( 1s \rightarrow 2p^\circ \) transition in more detail, since a combination of linear and quadratic Zeeman and diamagnetic effects ensures little sensitivity to \( H \) near 15 \( kG \) [48]. The quadratic Zeeman shift depends on the square of the magnetic quantum number \( m \), causing an uneven spacing of transition \( 1s \rightarrow 2p^\circ \) between \( 1s \rightarrow 2p^- \) and \( 1s \rightarrow 2p^+ \).

(Fig. 26) The dominant factor in setting the asymmetric shape of the sharp neutral donor inter-bound state absorption lines in GaAs, the lines show large paramagnetic splittings and diamagnetic shifts consistent with a near hydrogenic centre with low electron mass (from ref. [48]).
moments of the $1s$ and $2p^-$ states are equal and opposite, the quadrupolar contribution is quenched and the broadening is dominated by the quadratic Stark effect, i.e. the interaction of the electrostatic field of the charged centres with the induced dipole moment of the neutral donor. In total, for a transition between the $i$th and $j$th donor states, the local energy $\Delta \hbar \nu_{ij}$ is given by

$$\Delta \hbar \nu_{ij} = E_i - E_j - \frac{1}{4} (Q_i - Q_j) \frac{1}{j z} f_z - e^2 [(C^+_1 - C^+_0) F^+_1 + (C^-_1 - C^-_0) F^-_1]$$

where the $E_i$ are the energies of the unperturbed states, the $Q_i$ are quadrupole moments, the $F_i$ are components of the electric field parallel and perpendicular to the magnetic field which defines the direction $z$ and the coefficients $C$ represent directional averages of the electrostatic interaction for the quadratic Stark effect and contain the polarizability of the neutral donors. The detailed evaluation of lineshape using this primary equation is complicated by the treatment of the spatial statistics of the electric field. Besides affecting the linewidths, the internal electric field couples the $2s$ and $2p^0$ donor states, breaking the parity selection rule against $1s \rightarrow 2s$ photoexcitation [50]. The reduction of linewidth with field due to the quenching of the quadrupolar component is clearly shown in figure 26. Vapour phase epitaxial sample 1 is doped near $10^{14}$ cm$^{-3}$ with $\sim 90 \%$ compensation, sample 2 is doped near $3 \times 10^{14}$ cm$^{-3}$ with $\sim 70 \%$ compensation.

(Fig. 27) These effects conspire to make it convenient to examine the very small chemical shifts for donors in GaAs from the $1s \rightarrow 2p^-$ photoexcitation peaks at fields $15 \rightarrow 20$ kG. I show some spectra obtained recently by Stradling et al. [51], in which several donor species have been identified through studies of appropriately doped samples. The total spread in chemical shift is $< 1$ cm$^{-1}$ or $\sim 0.1$ meV, appreciably smaller than reported in an early study on inadequately refined GaAs [52]. These small chemical shifts are a direct consequence of the small contact interaction between the donor core and the electron wavefunction even in the $1s$ ground state, where $a_0 \sim 100$ Å.

(Fig. 28) Is intended to show that by no means all is known about the optical spectra in GaAs, even for those few major impurities discussed in this talk. The band labelled Si? is a characteristic of Si-doped InGaAs and is associated with the well-known 0.1 eV deep acceptor upon which the efficient operation of heavily Si-doped GaAs LEDs depends [53]. Despite
this device interest, the exact nature of the Si-related centre responsible for this band is unknown. Note that 
the strength of LO phonon coupling is about 100 times 
larger than in the doublet (F → B and D-A pair) asso-
ciated with the isolated Si$_{as}$ acceptor, discussed above. 
Coupling to acoustical phonons is also strong for the 
lower energy band, to the extent that the F → B and 
D-A pair contributions, which presumably exist, 
cannot be separated. The Si$^-$ spectrum is superficially 
similar to that reported by Cho and Hayashi [54] from 
molecular beam epitaxial GaAs : Si. However, these 
authors found it specific to material prepared under 
As-excess conditions, which is inconsistent with the 
usual findings for the 0.1 eV acceptor in GaAs : Si, 
namely that it is seen in LPE material, but not for melt 
grown or VPE crystals [55]. On the other hand, like the 
mbe but unlike previous reports of LPE GaAs : Si, the 
spectrum in figure 28 was obtained at a relatively low 
concentration of Si, $N$$_{A}$/ $N$$_{D}$ ~ $1 \times 10^{13}$ cm$^{-3}$. It has 
been suggested that this 0.1 eV acceptor is connected 
with the simple associate Si$_{as}$Si$_{as}$ [56]. However, 
this associate is a (molecular) isoelectronic centre, not 
an acceptor. Further, this particular isoelectronic centre 
is not expected to possess a bound state, since $E_A + E_D$ 
is only ~ 40 meV for Si in GaAs. Impurity phonon 
studies indicate that GaAs : Si contains much more 
complex Si associates, in addition to this simple 
form (Newman, R., private communication and refe-
rence [5]).

The behaviour of Si in GaAs is further complicated 
by the presence of an even broader photoluminescence 
band peaking near 1.18 eV at 77 K, exceptionally 
strong in heavily Si-doped VPE GaAs [55]. It is not 
clear whether this is the same as the peak reported 
near 1.22 eV in mbe GaAs [54] at 80 K for a total Si 
concentration $\geq 5 \times 10^{18}$ cm$^{-3}$. A 40 meV shift in 
such a broad band could readily result fortuitously 
from differences in recording conditions in uncorrected 
photoluminescence spectra. The VPE work suggested 
that this band involves a Si associate containing some 
unknown impurity, while the mbe work confirmed 
that this band is very strong in heavily-doped GaAs : Si 
grown under As-rich conditions. Evidently, much 
additional work will be needed to establish the centres 
responsible for even the dominant photoluminescence 
of GaAs : Si. A close interaction between photo-
luminescence and impurity phonon spectroscopy 
should yield dividends in this difficult task, given that 
the photoluminescence spectra are devoid of helpful 
detail.

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White for the very recent work on acceptors in GaAs. 
As ever, I am grateful to the many skilled crystal 
growers with whom I have had the fortune to collabo-
rate. Their skill forms the essential basis of any 
improvement in our understanding of the physics of 
impurities in semiconductors.

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DISCUSSION

Y. MARFAING. — May the Haynes’ rule be extrapolated to deep centers?

P. J. DEAN. — A variety of recent work has shown that the Haynes’ rule is much more complex than has been supposed hitherto. The spectra of excitons bound to neutral donors and acceptors in GaP show that although $\Delta E_{R} \neq E_{A}$, $E_{DA}$, the straight lines representing this trend do not pass near the point $E_{R} = E_{DA} = 0$. Unfortunately, luminescence of excitons bound to very deep centres such as the donor O$_{D}$ or acceptor S$_{A}$ has not been identified, so experimental extrapolation of Haynes’ rule to very deep centres has not been obtained. The strength of the relevant no-phonon lines is predicted to be low for such luminescence, both because of strong electron-phonon interaction and particularly as a result of very strong Auger recombinations. The work on excitons bound to neutral acceptors in GaAs described in this talk, as well as some other experimental indications, suggests that extrapolation of Haynes’ rule data obtained for nearly effective mass-like centres to centres with much larger binding energy is a very dangerous procedure. Hayne’s plot is very puzzling for acceptors in GaAs (and InP). $E_{A}$ is nearly independent of $E_{A}$ over the whole range of $E_{A}$, we observe (roughly comparable to the range of central cell corrections observed for simple acceptors in Si and GaP). Indeed, $(E_{A})_{Ge} < (E_{A})_{Zn}$, although $(E_{A})_{Ge} > (E_{A})_{Zn}$! On the other hand, we know that $E_{A}$ eventually increases with $E_{A}$ when the latter is very large, for example for (Sn)$_{As}$. Thus, Hayne’s rule curve is very non-linear (and even non-monotonic) in GaAs and InP and can only be determined empirically at present.

H. KRESSEL. — You show a value for the ionization energy of Si$_{As}$ which is larger than the value reported by Williams some years ago. Is the difference due to a higher purity in your crystals?

P. J. DEAN. — The Si data were obtained primarily from very lightly back-doped lpe crystals. These crystals were grown by P. D. Greene at STL labs in a system which gave $(N_{D} - N_{A})$ in the low $10^{13}$ cm$^{-3}$ range with noadvertent doping. With progressive addition of Si, the material become p-type in the $10^{14}$-$10^{15}$ cm$^{-3}$ range. The three free-to-bound peaks in the edge luminescence transformed to a single band identical in spectral position to the central member of the original three. Similarly, though the undoped material showed two sharp two-hole bound exciton replicas, only one of these persisted in the Si-doped material (the two-hole replica of the Ge exciton is intrinsically ill-defined, we believe due to strong coupling of the relevant hole transition and the optical phonon). We clearly distinguish between Zn and Si in these optical data, and are certain that $(E_{A})_{Si} > (E_{A})_{Zn}$.