Bound-Exciton, Free-Exciton, Band-Acceptor, Donor-Acceptor, and Auger Recombination in GaAs

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The broad-band photoluminescence spectra typical of bulk-grown or low-purity epitaxial GaAs breaks into a number of sharp emission lines in very-high-purity GaAs. At low temperatures (~2°K), emission peaks due to free excitons (1.5156 eV), excitons bound to neutral (1.5145 eV) and ionized (1.5133 eV) donors, and excitons bound to neutral (1.5125 eV) and ionized (1.4886 eV) acceptors are identified. Also, band-acceptor (1.4926 eV) and donor-acceptor (1.4857 eV) recombination is observed. The assignments are based on dependence of the emission lines with temperature, impurity content, and carrier type (n- or p-type material), as well as on the relative energy positions. The temperature dependence of the exciton–neutral-donor complex appears to be influenced by nonradiative Auger recombination.

I. INTRODUCTION

PHOTOLUMINESCENCE edge emission of n- and p-type high-purity GaAs reveals considerable structure not previously resolved in the emission bands of bulk-grown GaAs.[1] Earlier investigations on impure materials have shown the existence of exciton recombination[2] and donor-acceptor recombination[3] replicated by the LO phonon energy.

In the present work we find, at very low temperatures, a high-energy group of lines around 1.5 eV interpreted as arising from free excitons, and excitons bound to ionized and neutral donors, while a lower-energy group of emission lines around 1.49 eV is identified as consisting of band-acceptor and donor-acceptor recombination. An additional emission line is tentatively attributed to excitons bound to ionized acceptors. The temperature dependence provides evidence for Auger nonradiative decay of the exciton–neutral-donor complex. Further, the dependence of the emission on the impurity concentration reveals the donor-acceptor recombination emerging from a weak sharp line to become the dominant recombination mechanism at higher impurity concentrations. This is accompanied by a very strong quenching of the exciton-donor complex.

II. SAMPLES

Fifteen n- and p-type vapor-grown epitaxial samples have been studied. None of the samples was intentionally doped. However, they were all grown in SiO_2 reactors, so both Si and O are expected as contaminants.[4] Si can enter GaAs substitutionally for either Ga or As to produce, respectively, a donor or acceptor impurity. It is known that the preferred site of Si depends on the growth conditions. For example, on increasing As pressure during growth, it is observed that the samples have an increased tendency to become p type. Similar variations are obtained by altering the growth temperature, a fact sometimes used in growing GaAs diodes with Si as the major impurity in both the n and p regions.[5] Comparison of the photoluminescence spectra of solution-regrown epitaxial GaAs intentionally doped to increased concentrations of Si indicates that Si is in fact the dominant (both donor and acceptor) impurity in the undoped samples investigated. All of the samples were obtained in an effort to grow high-purity GaAs. The different impurity concentrations of the samples represent the varying degrees of success in this effort.

The impurity content is estimated from comparison of the Hall (van der Pauw) and conductivity mobilities over wide temperature ranges.[6] Representative changes in the photoluminescence spectra attributed to the changes in the Si concentrations as estimated from the electrical measurements are illustrated in Fig. 1. Other anticipated impurities such as O or Cl may be present but are not identified as contributing to the observed spectra in this wavelength range. Also, spectra induced by doping with other acceptor impurities, Cd, Mg, or Zn, are quite different. For these reasons, we assume that the entire impurity spectra from these samples arises from Si. This assumption limits to eight the number of principal emission lines reasonably expected, namely, the free exciton, four lines arising from excitons bound to ionized and neutral donors and acceptors, direct band to impurity recombination (donors and acceptors), and donor-acceptor recombination. In relatively pure materials, six (and sometimes seven) of

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[1] E. H. Bogardus, H. B. Bebb, and R. A. Reynolds, Bull. Am. Phys. Soc. **13**, 497 (1968).

[2] M. I. Nathan and G. Burns, Phys. Rev. **129**, 125 (1963).

[3] R. C. C. Leite and A. E. DiGiovanni, Phys. Rev. **153**, 841 (1967), first provided firm evidence for the importance of (D-A) recombination in GaAs which could be interpreted in terms of the Coulomb interaction e^2/KR. J. H. Yee and G. A. Condas, J. Appl. Phys. **39**, 351 (1968), supported this conclusion. Earlier, however, G. Lucovsky, A. J. Varga, and R. F. Schwartz, Solid State Commun. **3**, 9 (1965), suggested that the 1.49-eV emission could be interpreted in terms of (D-A) recombination, assuming sufficient donor concentration to cause banding.

[4] R. W. Conrad, R. A. Reynolds, and M. W. Jeffcoat, Solid-State Electron. **10**, 507 (1967).

[5] H. Ruppert, J. M. Woodall, K. Konnerth, and D. G. Petit, Appl. Phys. Letters, **9**, 221 (1966); see also W. Spitzer and W. Allred, *ibid.* **12**, 5 (1968).

[6] R. A. Reynolds, Solid-State Electron. **11**, 385 (1968); and (private communication).

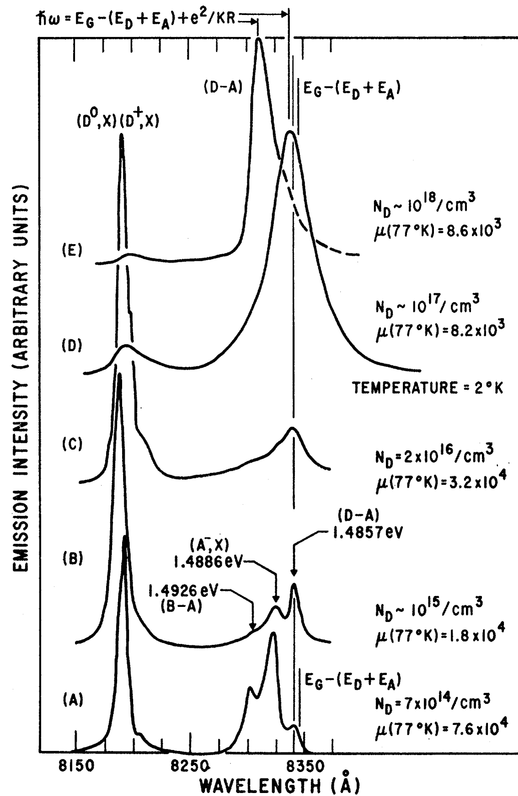


FIG. 1. Concentration dependence of n-type GaAs illustrating the changes in the emission with impurity content. Particularly striking are the quenching of bound-exciton complex with increasing impurity concentration and the increase in intensity and energy shift of the donor-acceptor (D-A) recombination with increasing impurity concentration.

the eight lines are observed at low temperatures. Additional lines are observed in some samples, but they are attributed to foreign trace impurities because of their tenuous appearance. The spectra attributed to Si are quite persistent in all samples.

III. BACKGROUND

In order to place the present work in the proper perspective, we briefly review what is known. Figure 2 schematically displays the energy positions of the emission lines that are theoretically expected to occur for relatively pure GaAs containing one type of shallow acceptor and one type of shallow donor, e.g., Si. Other emission lines are also possible, such as phonon replicas and emission from excited excitonic states, but they should generally be less intense. The major emission lines are expected to arise from excitons: either free excitons, excitons trapped on neutral or ionized impurities, or excitons trapped on impurity pairs (donor-acceptor recombination).

Sturge[7] has identified the free exciton in GaAs in absorption. At low temperatures, the $n=1$ exciton absorption is very prominent at 1.5177 eV. In spite of its prominence in absorption, the free exciton was not identified in emission at low temperatures until very recently,[8] and then only in the highest-purity samples. Previous assignments of the 1.513-eV emission[2] characteristic of bulk-grown GaAs to free-exciton emission are in error. Inferences from more recent work[9,10] on high-purity material suggest that the 1.513-eV emission is due to shallow donors.

Since Haynes's[11] original observations in Si, radiative recombination due to excitons trapped on isolated neutral and ionized impurities has been studied in a wide variety of elemental and compound semiconductors. Recently, Sharma and Rodriguez have calculated the binding energies of excitons bound to ionized donor and acceptor impurities and to neutral donors.[12] References to relevant experimental work are given by these authors. Their detailed variational calculations modify to some extent Hopfield's[13] earlier estimates of the binding energies but are in substantial agreement in regions where both calculations are valid. The main conclusion of Sharma and Rodriguez is that excitons can be bound to both ionized donors and ionized acceptors in the same material, contrary to Hopfield's more approximate calculations. Assuming an effective-mass ratio $\sigma=m_e/m_h=0.15$ appropriate to GaAs, they predict a binding energy for an exciton X trapped on an ionized donor, D^+, of $E_{XD^+}=1.06E_D$, where E_D is the binding energy of an isolated donor D^0; for an exciton X trapped on an ionized acceptor A^- they find $E_{XA^-}=1.4E_A$. The binding energy for excitons bound to neutral impurities is usually expressed in terms of the dissociation energy D_0, i.e., the energy required to separate the complex into a neutral impurity and a free excition. For excitons bound to neutral donors D^0, Sharma and Rodriguez calculate a dissociation energy of $D_0=0.13E_D$, giving a binding energy of $E_{XD^0}=E_X+0.13E_D$ in reasonable agreement with Hopfield's estimate of $E_X+0.19E_D$. Here E_X is the binding energy of the free exciton. Sharma and Rodriguez have not considered the exciton–neutral-acceptor complex. Hopfield gives $E_{XA^0}=E_X+0.07E_A$ for this case. Collecting the results, we can estimate the photon emission energy $\hbar\omega$ of radiative annihilation of the exciton complexes (D^0,X), (D^+,X), (A^0,X), and (A^-,X):

$$\hbar\omega(X_{D^0})=E_G-E_X-0.13E_D\,, \qquad (1a)$$

$$\hbar\omega(X_{D^+})=E_G-E_D-0.06E_D\,, \qquad (1b)$$

[7] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[8] M. A. Gilleo, D. E. Hill, and F. V. Williams, Bull. Am. Phys. Soc. 12, 656 (1967).

[9] P. T. Bailey, M. A. Gilleo, and D. E. Hill, Bull. Am. Phys. Soc. 13, 497 (1968).

[10] M. A. Gilleo, P. T. Bailey, and D. E. Hill, Bull. Am. Phys. Soc. 13, 497 (1968).

[11] J. R. Haynes, Phys. Rev. Letters 4, 361 (1960).

[12] R. R. Sharma and S. Rodriguez, Phys. Rev. 153, 823 (1967); 159, 649 (1967).

[13] J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

$$\hbar\omega(X_{A^0}) = E_G - E_X - 0.07E_A\,, \qquad (1c)$$

$$\hbar\omega(X_{A^-}) = E_G - E_A - 0.4E_A\,. \qquad (1d)$$

From effective-mass arguments based on the hydrogenic model, we have $E_X = 4.4$ meV, $E_D = (1+\sigma)E_X = 5.2$ meV, and $E_A = E_D/\sigma = 34$ meV, assuming $\sigma = m_e/m_h = 0.15$ for GaAs. Obviously, in view of the complexity of the valence band structure these estimates are not quantitatively accurate. Our experimental results discussed below give $E_D = 6.8$ meV and $E_A = 29.7$ meV. Using these values together with $E_X = 4.4$ meV, Eqs. (1a)–(1d) give 1.515, 1.5133, 1.491, and 1.481 eV, respectively, for the emission energies. Rather than specifying these estimated energies in Fig. 2, we have recorded the energies actually observed to facilitate comparison with the data where the lines 1.5145, 1.5133, 1.4926, and 1.4886 eV are identified as annihilation of excitons trapped on neutral donors, ionized donors, neutral acceptors, and ionized acceptors, respectively.

Deviations from the predicted binding energies are to be expected in light of the approximations involved in the theory. Similar discrepancies between the calculated and measured binding energies for exciton complexes occur in nearly all systems that have been examined experimentally.[14,15] Actually, in the present instance it is possible to improve the agreement by altering the effective-mass ratio to a value of $\sigma = 0.2$. However, in view of the known discrepancies typical of other semiconductors, e.g., Si, SiC, and GaP, it is difficult to justify altering σ from previously reported estimates[16] in order to obtain quantitative agreement between calculated and observed binding energies of bound-exciton complexes.

Emission due to excitons bound to donor-acceptor pairs, (D^+A^-X) or $(D\text{-}A)$, has been investigated extensively in several materials. Particularly striking is the well-known donor-acceptor-pair spectra in GaP consisting of up to several hundred sharp lines. In GaAs, the small binding energies of the impurities place the sharp-line emission above the band gap. Only the broad-band emission due to very distant donor-acceptor pairs is expected to be observable. A broad-band emission near 1.49 eV (at 4.2°K) characteristic of undoped bulk-grown GaAs has been interpreted as distant donor-acceptor recombination from its dependence on temperature and excitation intensity in accord with the well-known relation[3]

$$\hbar\omega = E_G - E_A - E_D + e^2/KR\,. \qquad (2)$$

Impurity concentrations in bulk-grown samples are of the order of 10^{18} cm^{-3}; it is perhaps not surprising

[14] P. J. Dean, Phys. Rev. **157**, 655 (1967).

[15] D. R. Hamilton, W. J. Choyke, and Lyle Patrick, Phys. Rev. **131**, 127 (1968).

[16] O. Madelung, *Physics of III–V Semiconductors* (John Wiley & Sons, Inc., New York, 1964), p. 352.

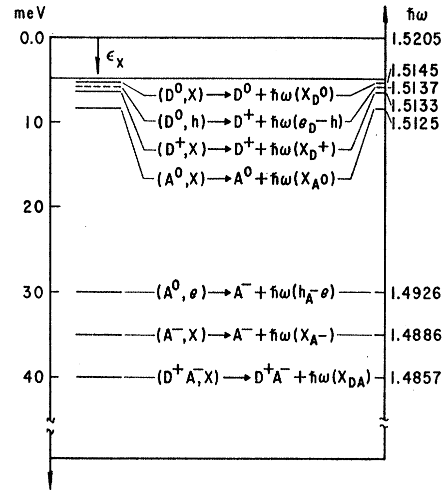


FIG. 2. Bound- and free-exciton emission energies for GaAs containing one species of donor impurities and one species of acceptor impurities. The band gap is estimated as 1.5205 eV from the observed position of the free exciton at 1.5161 eV (not labeled in figure). The energies of the exciton-neutral donor (D^0,X), neutral donor-band (D^0,h), exciton-ionized donor (D^+,X), and exciton-neutral acceptor (A^0,X) emissions at 1.5145 eV, 1.5137 eV, 1.5133 eV, and 1.5125 eV have been adjusted slightly from the theoretically predicted values to correspond with the measured values. Similar small adjustments are made for the band-acceptor (A^0,e), exciton-ionized acceptor (A^-,X), and donor-acceptor (D^+,A^-,X) recombination energies. None of the energy shifts extends outside reasonable theoretical uncertainties.

that interimpurity [i.e., $(D\text{-}A)$] transitions dominate when they occur in such heavy concentrations. Narrow emission lines arising from conduction-band to acceptor transitions (A^0,e) and from excitons bound to ionized acceptors (A^-,X) have not been identified in bulk-grown materials [compare Figs. 1(D) and 1(A)].

Epitaxial GaAs offers the possibility of lower residual impurity concentrations so that other radiative mechanisms can be observed. Radiative recombination involving acceptors in cadmium-doped epitaxial GaAs has been firmly identified as recombination of free (conduction-band) electrons with neutral acceptors. The assignment is based on the emission energy dependence on impurity doping, the temperature dependence of the radiative lifetime,[17] and the temperature dependence of the line shape.[18] The empirical results for all of these parameters are in quantitative agreement with the theory for free-electron-to-neutral-acceptor recombination. For example, the line shape is accurately described over a wide temperature range as arising from the thermal distribution of free carriers as derived by Eagles and Dumke.[19] This type of free-carrier broadening is not consistent with bound-exciton or donor-acceptor recombination. Similar but less exten-

[17] E. W. Williams and R. A. Chapman, J. Appl. Phys. **38**, 2547 (1967).

[18] H. B. Bebb and E. W. Williams, Bull. Am. Phys. Soc. **13**, 26 (1968); also (unpublished).

[19] D. M. Eagles, J. Phys. Chem. Solids **16**, 76 (1960); W. P. Dumke, Phys. Rev. **132**, 1998 (1963).

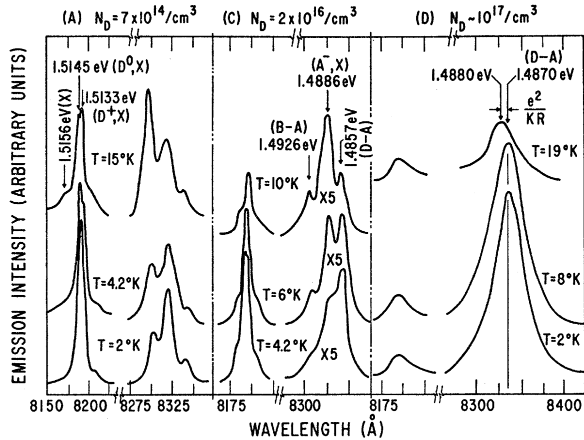


FIG. 3. Temperature dependence of n-type GaAs showing in (A) the increase in intensity of B-A with a simultaneous decrease in (D^0,X). In (C) the D-A line decreases rapidly with increased temperature as the electrons from (D^0,X) funnel into the B-A peak. While the increase in the $(B$-$A)$ peak for sample (C) appears much less dramatic than for sample (A), its actual rate of change is approximately the same and behaves as illustrated in Fig. 6. In (D) the shift in the D-A line at higher temperatures, as a result of the smaller average separation between donors and acceptors, is apparent. This shift is not seen in higher purity samples such as (A) or (C).

sive studies have been made for other impurity dopings, in particular Si-doped GaAs.[18]

Very recently, emission due to free excitons, excitons bound to neutral and ionized Se donors, and excitons bound to neutral and ionized Zn acceptors has been reported.[10] The data were taken below 4.2°K from doped high-quality epitaxial GaAs. In the present paper we investigate similar bound-exciton complexes involving Si donors and acceptors in "as-grown" epitaxial GaAs. In addition to previously reported observations,[10] emission lines due to free-electron-to-acceptor recombination (A^0,e) and donor-acceptor recombination (D^+A^-X) are identified as coexisting with the bound exciton ionized acceptor (A^-,X) line to form a triplet of lines near 1.49 eV. Further, the dependence of radiative recombination on temperature, impurity concentration, and the majority carrier (n- and p-type samples) has been studied.

Of the emission lines anticipated in Fig. 2, only one of the emission lines expected for the exciton-donor complex is not at least tentatively observed in the emission spectra of high-purity GaAs. If we accept the identification previously given[10] as excitons bound to neutral and ionized donors, then the missing line is the neutral-donor–free-hole recombination. For ease of presentation we will temporarily accept this identification. Later, however, we will consider the possibility that the two donor-involved lines present are excitno-neutral-donor (D^0,X) and neutral-donor–free-hole (D^0,h) recombination, and that the exciton–ionized-donor (D^+,X) emission is the emission line that is absent.

IV. EXCITON-DONOR COMPLEX

The low-temperature spectra of relatively pure n-type GaAs is often dominated by a complex of excitons consisting of the free-exciton emission at 1.5156 eV [usually weak at low temperatures $\sim$2°K; see Figs. 1(A) and 3(A)], a line at 1.5145 eV attributed to excitons bound to neutral donors, which we denote (D^0,X), and the partner line at 1.5133 eV attributed (for now) to excitons bound to ionized donors, denoted (D^+,X). Another line at 1.5125 eV is sometimes weakly present in n-type GaAs. In p-type material it becomes a prominent line, suggesting that it may arise from neutral acceptors. The behavior of this line is consistent with the exciton–neutral-acceptor complex (A^0,X), which is discussed below at greater length.

The *free-exciton* line at 1.5156 eV is identified from its energy position and line shape. For temperatures exceeding 15°K, the measured exciton line shape agrees well with that predicted from Sturge's absorption measurements[7] using detailed balance arguments $R(\hbar\omega)\sim(\hbar\omega)^2\alpha(\hbar\omega)\exp(-\hbar\omega/KT)$ after a correction for self-absorption has been included. Here $\alpha(\hbar\omega)$ is the absorption coefficient and the other terms have their usual meaning. Our photoluminescence results suggests a band gap of $E_G=1.5205$ eV, assuming the calculated exciton binding energy of $E_X=4.4$ meV. This places the $n=1$ exciton line seen in absorption at 1.5161 eV (rather than the 1.5177 eV measured by Sturge). Because the Boltzmann factor emphasizes the low-energy side of the finite width of the $n=1$ exciton line, the emission is shifted to slightly lower energies with a peak at 1.5156 eV. Our values agree well with those of Bailey, Gilleo, and Hill[9] based on the observation of both the $n=1$ and 2 exciton lines, and the direct band-to-band recombination at 1.4°K. The very small discrepancies are resolved if the finite width of the $n=1$ line measured by Sturge is substantially reduced as might be expected in the higher purity samples. Then the shift we find between absorption and emission would not occur.

Each donor impurity gives rise to two *bound-exciton* emission lines, the neutral-donor–exciton emission (D^0,X) just below the free-exciton line and the ionized-donor–exciton emission (D^+,X) just under E_G-E_D. The assignment of the 1.5133-eV emission and the 1.5145-eV emission to (D^+,X) and (D^0,X), respectively, is energetically consistent with Eqs. (1a) and (1b). Assuming the band gap of 1.5205 eV estimated from the free-exciton emission, Eqs. (1a) and (1b) can be used to estimate the donor binding energy as $E_D=6.8$ meV.

Additional evidence for assignment of the bound-exciton lines is obtained from the dependence of the emission intensities on temperature and compensation. In p-type material, the donors are ionized and formation of the neutral-donor complex (D^0,X) can occur only by trapping minority carriers. Thus, the (D^+,X)

line might be expected to increase in intensity relative to the (D^0,X) line in changing from n- to p-type material. This reversal in relative intensities is apparent for the 1.5145-eV and 1.5133-eV lines from Fig. 4. Further, both of these "donor lines" occur more weakly in p-type material, while the 1.5125-eV line emerges as a prominent (if not dominant) line consistent with its assignment to a neutral-acceptor–exciton complex (A^0,X).

The temperature dependences (for $2<T<10°K$) of the (D^0,X) 1.5145-eV and (D^+,X) 1.5133-eV emission lines are quite different. Qualitatively [see Fig. 3(a)], the (D^0,X) emission decreases rapidly as the temperature is increased from 2 to 10°K, while the (D^+,X) line remains essentially constant over this temperature region. Quantitative results are difficult to obtain because of the obvious interaction between the two lines. An attempt to estimate the intensities of the individual components is made by approximating the line shapes with triangles adjusted to the proper half-widths. By plotting (or calculating) the intensities of the composite line as a function of the relative intensities of the two components, the relation between the components and the composite can be estimated. In fact, the degree to which the emission lines are approximated by triangular shapes suggests that much of the broadening arises from the spectrometer. (The convolution of the entrance and exit slits is a triangle.) A check of this possibility revealed that up to 30% of the linewidth could be instrumental in the sharpest lines. Some uncertainty in the low-temperature data is consequently expected.

Figures 5 and 6 plot the integrated intensities of the (D^0,X), (D^+,X), and (A^0,e) emission components as a function of temperature for sample (A) indicated in Figs. 1(A) and 3(A). Figure 3(A), of course, shows the composite line, while Figs. 5 and 6 are plotted from the component intensities estimated from assuming triangular line shapes discussed above. Hence, in comparing the figures, the resolution into separate components must be taken into account. Last, it is well known that interacting lines are displaced toward each other as well as altered in intensity. For these very narrow lines, the displacement is small and apparently occurs only when the peaks are not completely resolved [compare Figs. 3(A) and 4].

The temperature dependence of the (D^+,X) emission line can be described by[14]

$$I(T)=I(T=0)/[1+C\exp(-E_T/KT)] \qquad (3)$$

over the entire temperature range measured ($2<T<30°K$). $I(T=0)$ is the intensity, as $T=0$, and C is a temperature-independent constant related to the Fermi level.[20] The thermal binding energy E_T is given by the slope of the straight-line portion of Fig. 5 as 7.0 meV.

[20] J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962), p. 130.

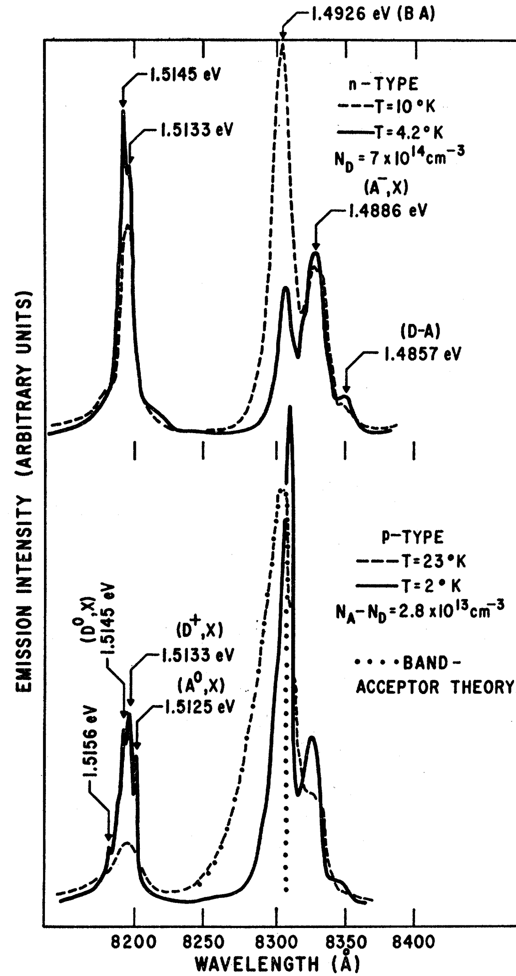
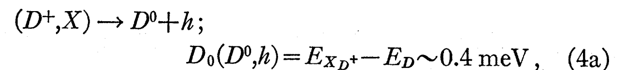
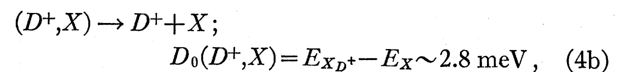


FIG. 4. Comparison of typical photoluminescence spectra from n- and p-type GaAs. The intensities of 1.5145-eV and 1.5133-eV lines are reduced by a factor of about 100, relative to the acceptor lines in going from n- to p-type material, apparently excluding the possibility that either of the lines can be attributed to excitons bound to neutral acceptors. The emission peak at 1.5125 eV emerges in p-type material as a prominent line consistent with its assignment to an exciton bound to a neutral acceptor. It is occasionally seen very weakly in n-type material. The emission at 1.4926 eV becomes the dominant line in p-type material, suggesting it as a candidate for band-neutral acceptor recombination. Line-shape comparisons between the simple Eagle's theory (Ref. 19) and experiment for several temperatures confirms this assignment. One such comparison for $T=23°K$ is shown as an example of the agreement.

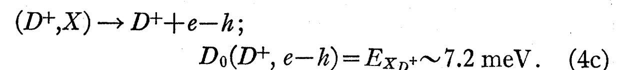
Three dissociation paths are available to the (D^+,X) complex, each involving a different activation energy D_0:



$$(D^+,X)\to D^0+h;\quad D_0(D^0,h)=E_{X_{D^+}}-E_D\sim 0.4\text{ meV}, \qquad (4a)$$



$$(D^+,X)\to D^++X;\quad D_0(D^+,X)=E_{X_{D^+}}-E_X\sim 2.8\text{ meV}, \qquad (4b)$$



$$(D^+,X)\to D^++e-h;\quad D_0(D^+,e-h)=E_{X_{D^+}}\sim 7.2\text{ meV}. \qquad (4c)$$

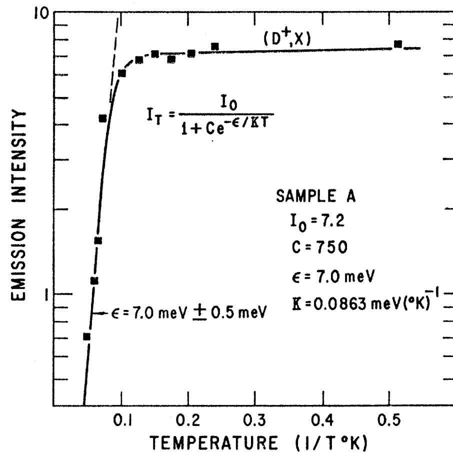


FIG. 5. Comparison of the measured temperature dependence (squares) of the 1.5133-eV (D^+,X) emission and the temperature dependence predicted (solid line) from Eq. (3), assuming a single activation energy of $\epsilon=7.0$ meV, which is approximately equal to the donor binding energy.

The dissociation energies D_0 are obtained directly from Fig. 2. Dissociation of the (D^+,X) complex into a neutral donor (D^0) and free hole (h), or into an ionized donor (D^+) and a free exciton (X), involve small activation energies which are not consistent with the data. Thus, if the 1.5133-eV line is ascribed to the (D^+,X) complex, it appears that the complex thermally dissociates into an ionized donor (D^+) and a free-electron–hole pair $(e-h)$ with an activation energy of 7.2 meV. The liberation of free carriers can be expected for neutral-donor–exciton complexes under certain conditions[14] but is more difficult to explain for the ionized-donor–exciton system presently under consideration. Perhaps it is more meaningful to consider the temperature dependence of the capture rate of excitons by ionized donors or holes by neutral donors involved in forming the exciton-impurity complexes. In particular, if the (D^+,X) complex is formed through the agency of neutral donors trapping holes, then the number of (D^+,X) complexes formed would be proportional to the number of neutral donors (D^0); the number of neutral donors at temperature T should obey a relation like Eq. (2). This still does not explain why the small dissociation energies, $D_0(D^0,h)\simeq 0.4$ meV and $D_0(D^+,X)\simeq 2.8$ meV, do not appear as thermal activation energies.

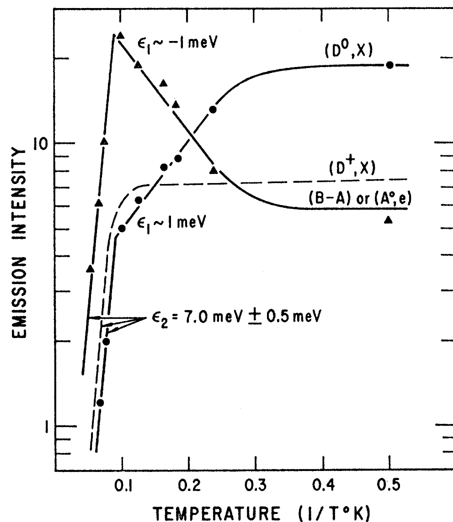


FIG. 6. Temperature dependence of the exciton–neutral-donor complex (D^0,X) and band-acceptor (A^0,e) recombination. The correlation of the decrease in (D^0,X) with the increase in (A^0,e) is apparent, suggesting liberation of free electrons by (D^0,X) which recombine with neutral acceptors, causing the increase in (A^0,e) in the low-temperature region below $1/T\simeq 0.1$ or $T\simeq 10$°K. Above 10°K all three emission lines [the (D^+,X) emission shown in Fig. 5 is reproduced as the dashed line here] decrease at a rate corresponding to a thermal activation energy of $\sim$7.0 meV equal to the donor binding energy.

Alternatively, the observed temperature dependence is easily understood if the 1.5133-eV emission line is a band-to-neutral-donor impurity transition $D^0+h\rightarrow \hbar\omega+D^+$ rather than an exciton–ionized-donor transition $(D^+,X)\rightarrow \hbar\omega+D^+$, since again the number of neutral donors should follow the temperature dependence of Eq. (3). Further, assignment of the 1.5133-eV line to (D^0,h) actually brings the energy relations in Eqs. (1) into better accord than the (D^0,X) assignment. However, we again stress that the calculated energies are not expected to be quantitatively accurate and should not be used in selecting between such small differences. It might be argued that thermal broadening arising from the kinetic energies of the free carriers should be apparent in band-to-impurity transitions. However, the very shallow donors in GaAs are diffuse and hence possess nonvanishing Fourier coefficients over a very small portion of $\mathbf{k}$ space around $\mathbf{k}=0$.[21] Assuming momentum-conserving transitions, only holes near $\mathbf{k}=0$ (small kinetic energy) can optically recombine with the electrons trapped on the donor. Within the hydrogenic model this limits the thermal broadening to about 0.5 meV for donors in GaAs ($KT\sim 0.5$ meV at about 6°K).[18] Thus, the linewidth anticipated for the (D^0,h) emission is comparable to that of the "sharp" bound-exciton lines. Our data are therefore consistent with either assignment of the 1.5133-eV line. Indeed, the temperature dependence favors the (D^0,h) assignment. However, previous assignments of emission lines ascribed to donors have referred to only the bound excitons (D^+,X) and (D^0,X).[8,10] Our data do not completely rule out the assignment of the 1.5133-eV line to the (D^+,X) complex; therefore, we maintain this notation for compatability with previous work. We wish to make clear, though, that we favor the alternative interpretation of band–neutral-impurity (D^0,h) emission, which in any case is just an excited (continuum) state of the (D^+,X) system.

[21] W. Kohn, *Solid State Physics* (Academic Press Inc., New York, 1957), Vol. 5, p. 281.

From Fig. 6, two separate processes appear to be active in determining the temperature dependence of the 1.5145-eV (D^0,X) emission line. In the low-temperature region below 10°K, the temperature dependence of the emission can again be described by Eq. (2), taking an activation energy of $E_T \simeq 1$ meV. Above 10°K, a second process with an activation energy of about 7.0 meV becomes dominant. Like the (D^+,X) system, the (D^0,X) complex can thermally dissociate by several processes involving different dissociation (or activation) energies:

$$(D^0,X) \rightarrow D^0+X; \quad D_0(D^0,X)=E_{XD^0}-E_X \sim 1.0 \text{ meV}, \quad (5a)$$

$$(D^0,X) \rightarrow (D^+,X)+e; \quad D_0(e)=E_X+D_0(D^0,X)-D_0(D^0,h) \sim 6.0 \text{ meV}, \quad (5b)$$

$$(D^0,X) \rightarrow D^+ + e; \quad D_0 \text{ (Auger recombination)} \simeq ?. \quad (5c)$$

Hamilton, Choyke, and Patrick have considered the first two dissociation paths[15] in SiC. Dean found that in GaP the (D^0,X) complex dissociated with the liberation of a free electron as expected from comparing bound- and free-exciton binding energies in GaP.[14] In the present case of GaAs, (D^0,X) is expected to dissociate into a free exciton and neutral donor with a thermal activation energy equal to the dissociation energy $D_0(D^0,X) \sim 1.0$ meV. From Eq. (5b), $D_0(e)$ can be smaller than $D_0(D^0,X)$ only if $D_0(D^0,h)/E_X > 1$, which is far from the situation in GaAs. Comparing Eqs. (5a) and (5b), $D_0(e) \gg D_0(D^0,X)$, we see that it is not plausible that the (D^0,X) complex should thermally liberate a free electron.

Nevertheless, in the low-temperature region below 10°K, a rapid decrease of the intensity of the (D^0,X) line with increasing temperature is accompanied by just as rapid an increase in the emission line identified as conduction band to neutral acceptor (A^0,e). This effect, which appears from the raw data to be most dramatic for the highest-purity samples showing complete carrier "freezeout" such as sample (A), is seen qualitatively in Fig. 3(A) or more precisely in Fig. 6. In this temperature region, thermal ionization of the acceptors (or even shallow donors) cannot be important. The intensity changes indicate that the bound-exciton–neutral-donor (D^0,X) system thermally dissociates by ejecting into the conduction band a free electron which subsequently recombines with a neutral acceptor. From Fig. 6, this process involves a thermal activation energy of the order of 1 meV. As we have discussed above, such a small activation energy is not consistent with the liberation of free carriers.

Nonradiative Auger recombination provides a mechanism for this process. The (D^0,X) complex involves two electrons and a hole localized at the donor ion. One of the electrons can recombine with the hole, giving energy to the remaining electron rather than to the radiation field; the remaining electron is consequently ejected deep into the conduction band. These ejected electrons should thermalize very rapidly, attaining a thermal distribution before optically recombining with the acceptors. It is emphasized that at these low temperatures the only electrons in the conduction band come from either the exciting mercury lamp or by (Auger) ionization of the (D^0,X) complexes. Hence, the increase in the number of electrons in the conduction band by Auger recombination of the (D^0,X) systems can be significant.

Auger recombination is thought to be an important process for excitons bound to neutral donors in GaP and Si.[22] In these materials the lifetime measurements of the (D^0,X) emission are not consistent with the optical transition probabilities determined from absorption measurements. Order-of-magnitude estimates of the ratio of the Auger recombination rate to the radiative recombination rate indicate that the Auger rate is about 10^3 larger than the radiative process, roughly the measured discrepancy between absorption and emission rates in GaP. A similar ratio is calculated for GaAs. From this estimate, Auger recombination must be anticipated as an important process for the (D^0,X) in GaAs irrespective of experimental observations.

Unfortunately, the effects of finite temperatures on the Auger rates have not been considered. It is interesting that the thermal activation energy for Auger ionization of the (D^0,X) complex is essentially the energy required to dissociate the complex into a neutral donor and free exciton, $D_0(D^0,X) \sim 1$ meV. Thermal dissociation of (D^0,X) into a neutral donor D and free exciton X should cause an increase in the intensities of the free-exciton emission X at 1.5156 eV and the (D^0,h) or (D,X) emission lines. However, for $T < 10$°K, only the band-acceptor $(B\text{-}A)$ line increases coincidentally with the decrease in the (D^0,X) line, indicating Auger liberation of electrons. No increase in the number of free excitons is observed. It appears that the temperature dependence of Auger recombination in solids is an interesting theoretical problem.

For temperatures above 10°K, the emission intensities of the (D^0,X), (D^+,X), and (A^0,e) lines all decrease at the same rate, corresponding to an activation energy of $E_T(=7.0 \pm 0.5$ meV) equal to the donor binding energy. In n-type material these three emission intensities therefore all appear to depend on the number of neutral donors present at temperature T before optical excitation. The temperature variation of the number of neutral donors is given by an equation of the same form as Eq. (3), with the intensity I replaced by the concentration of donors. Upon exciting the sample with band-gap radiation, electrons and holes

[22] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters **17**, 1262 (1966), discuss Auger recombination of excitons bound to neutral donors in GaP and Si.

are generated in the bands. Some of these recombine to form free excitons. Neutral donors can then trap free excitons and holes to form (D^0,X) and (D^+,X) complexes in numbers proportional to the number of neutral donors available at temperature T. In the absence of an Auger process, the intensities of the (D^0,X) and (D^+,X) emission lines should correspond to Eq. (3), especially if we assign the 1.5133-eV line to neutral-donor–band recombination (D^0,h) as previously suggested. Some modification to Eq. (3) should occur by accounting for the different possible thermal dissociation paths involving activation energies smaller than the donor binding energy [see Eqs. (4) and (5)]. Still assuming the absence of an Auger process, it can be argued that the band-acceptor recombination should increase as temperature increases above 10°K, due to the increased number of electrons in the conduction band from donor ionization. The opposite intensity dependence is observed indicating that the dominant mechanism is quenched by thermal ionization of donors. Thus, the temperature variations of the (D^+,X), (D^0,X), and (A^0,e) emission lines are all somewhat surprising. The (D^+,X) emission is most easily understood if it is reassigned to (D^0,h). The correlation in the decrease of the (D^0,X) line with the increase of the (A^0,e) line for $T<10$°K, and the subsequent decrease in both lines above 10°K, corresponding to thermal ionization of neutral donors, is most easily explained by assuming a temperature-dependent Auger recombination of the (D^0,X) complex.

Evidence for liberation of free electrons by the (D^0,X) complex through the agency of the Auger process rests on the correctness of identifying the 1.492-eV emission line as band-acceptor (A^0,e) recombination. In the next section we consider emission lines involving acceptors.

V. EMISSION INVOLVING ACCEPTORS

The lower-energy group of lines near 1.49 eV apparent in Figs. 1, 3, and 4 are identified as band-to-acceptor (A^0,e) or $(B\text{-}A)$ recombination at 1.4926 eV, and donor-acceptor (D^+A^-X) or $(D\text{-}A)$ recombination at 1.4857 eV, and a tentative assignment of the 1.4886-eV emission peak to excitons bound to ionized acceptors (A^-,X).

The band-to-acceptor line is identified from its line shape, temperature dependence, and dependence on carrier type (n- or p-type material). For temperatures exceeding 15°K (up to 80°K), both the shape and change in position of the $(B\text{-}A)$ line are accurately predicted by the simple hydrogenic theory of Eagles,[19] $R(\hbar\omega)\sim y^{1/2}\exp(-y)$, where $y=(\hbar\omega-E_G+E_A)/KT$. With increasing temperature, the $(B\text{-}A)$ line broadens due to the thermal distribution $\exp(-y)$ of electrons in the conduction band. The other two lines do not broaden to the same extent. The maximum of $y^{1/2}\exp(-y)$ occurs at $y=0.5=(\hbar\omega-E_G+E_A)/KT$. Solving for E_A gives an acceptor binding energy of $E_A=28.7$ meV. At lower temperatures, $T<15$°K, other broadening mechanisms are operative, so that the observed width exceeds the width predicted from free-carrier motion. This, of course, is not surprising. Similar inhomogeneous broadening is also present in the other emission lines, e.g., free exciton. In relatively pure p-type material, the $(B\text{-}A)$ line emerges as the strongest line, as illustrated in Fig. 4. This increase in intensity is consistent with the increased number of neutral acceptors in p-type material. An example of the agreement between the simple theoretical curve $y^{1/2}\exp(-y)$ and experiment for the $(B\text{-}A)$ line in p-type material is indicated for $T=23$°K. $(B\text{-}A)$ transitions have been previously studied in high-purity GaAs,[17,18] and their nature is thought to be well understood. We believe the assignment of the 1.4926-eV emission line as a $(B\text{-}A)$ transition is quite firm.

The assignment of the 1.4886-eV line to the exciton–ionized-acceptor complex (A^-,X) is more tentative. It is roughly consistent with the calculations of Sharma and Rodriguez,[12] though it is somewhat closer to E_A than their results predict. In p-type samples it is weak compared to the $(B\text{-}A)$ line corresponding to the decreased number of ionized acceptors. It does not appear to be due to trace impurities, since it increases with the $(B\text{-}A)$ line upon doping with Si, and shows little sample to sample variation. Last, assignment of the line to $(B\text{-}A)$ or $(D\text{-}A)$ recombination is not consistent with the results presented here. Its behavior differs from either of these lines.

The $(D\text{-}A)$ recombination emission is almost unambiguously identified from consideration of only the data shown in Fig. 1. The broad-band spectra for the two higher-concentration samples is characteristic of the well-known spectra of bulk GaAs.[2,3] Both the observed concentration dependence shown in Fig. 1 and the temperature dependence shown in Fig. 3(D) are simply interpreted in terms of Eq. (2). Referring first to Fig. 1, we see that with decreasing impurity concentration, the average donor-acceptor separation, R, increases, and the emission energy shifts to lower energy, approaching [see Eq. (2)]

$$(\hbar\omega)_{\text{limit}}=E_G-(E_A+E_D) \quad \text{as} \quad R\rightarrow\infty\,.$$

As expected, the intensity also decreases with decreasing impurity concentration. In the higher-purity samples the $(D\text{-}A)$ emission becomes a weak component of the "acceptor complex." Since $E_G=1.5205$ eV, $E_A=28.7$ meV, and $E_D=6.8$ meV have already been determined, the limiting photon emission corresponding to the most distant pairs is determined by $(\hbar\omega)_{\text{limit}}=E_G-E_A-E_D=1.485$ eV, in close agreement to the observed limit, as illustrated in Fig. 1. For impurity concentrations below 5×10^{16} cm^{-1}, the peak of the $(D\text{-}A)$ emission remains near 1.4857 eV.

Thus, in relatively pure GaAs the average pair separation is sufficiently large that the Coulomb term e^2/KR remains small, and the traditional energy shifts in the emission energy $\hbar\omega$ as a function of temperature, excitation intensity, or concentration (below 5×10^{16}) are not observed. Only the intensity of the $(D\text{-}A)$ emission is altered, as illustrated in Fig. 3(C) and Fig. 1. For concentrations in excess of 10^{17} cm^{-3}, the $(D\text{-}A)$ emission band broadens and its position becomes dependent on temperature, as shown in Fig. 3(D), and concentration, as illustrated in Figs. 1(D) and 1(E), in the manner usually associated with $(D\text{-}A)$ recombination.[3]

Accompanying the increase in the $(D\text{-}A)$ recombination with increasing impurity concentration is a striking decrease of the "exciton-complex" emission. Two processes probably contribute to quenching: (i) the obvious increase in the donor-acceptor recombination, and (ii) the onset of nonradiative Auger recombination. Dean *et al.*[23] discussed a model for Auger recombination based on impurity banding while the present article was in preparation. According to their model, Auger nonradiative recombination becomes important when the donor impurity concentrations become sufficient for significant overlap between wave functions to occur. Then the interacting donors begin to spontaneously ionize by the Auger mechanism, quenching the donor-band radiative recombination. The Auger nonradiative recombination and donor-acceptor recombination should depend differently on concentration, providing a means to separate their contributions. However, in the undoped samples investigated, the residual donors and acceptors were in such ratios that both processes might reasonably be expected.

Figures 1(C) and 3(C) show the emission spectra of a sample of intermediate impurity. The exciton-donor complex emission is very strong, and the donor-acceptor emission is beginning to dominate the still very weak acceptor group of lines. As with the band-to-acceptor emission, the temperature dependence again reveals a correspondence between the 1.4857-eV $(D\text{-}A)$ emission intensity and donor-complex intensity. Both the "donor" emission and the $(D\text{-}A)$ emission show a marked decrease in intensity upon increasing the temperature from 2 to 10°K, corresponding to dissociation of donor-exciton complexes. Since thermal ionization should not occur in this temperature region for a defect center with a binding energy in excess of 30 meV corresponding to the emission energy of 1.4857 eV, we must conclude that this emission involves a donor, further supporting its assignment as $(D\text{-}A)$ emission. Additionally, the $(B\text{-}A)$ emission increases simultaneously with the decrease in the (D^0,X) and $(D\text{-}A)$ emission, corresponding to the increased number of free electrons in the conduction band. The change in $(B\text{-}A)$ intensity appears less dramatic in sample (C) than in the highest-purity sample (A). However, it still increases at the same rate between 2 and 10°K, corresponding to a thermal activation energy of 1 meV. The emission ascribed to (A^-,X) remains constant in intensity over a fairly wide temperature range, as expected for an acceptor line which is independent of shallow donor occupation.

VI. DISCUSSION

In this section we discuss possible alternative interpretations of the data and indicate which of our conclusions are firm and which are speculative.

Assignments of the three emission lines at 1.4926 eV, 1.4886 eV, and 1.4857 eV to $(B\text{-}A)$, (A^-,X), and $(D\text{-}A)$ are consistent with their predicted energy positions, and the observed intensity (and line shape) changes with temperature, impurity concentration, and majority carrier type (n or p). No variations inconsistent with any of these assignments were noted in any of the fifteen samples investigated.

Assignments of the higher-energy group of lines are made difficult by their small energy separations. From theory, the order of the energies of exciton-donor emission is certain, namely, (X), (D^0,X), (D^0,h), and (D^+,X). A complicating factor is the occurrence of the exciton–neutral-acceptor line (A^0,X) in the same energy region. Fortunately, the free-exciton and (D^0,X) emissions can be identified with reasonable certainty. However, an erroneous assignment could still occur if it happens that the (D^0,X) radiative recombination is completely quenched by nonradiative Auger recombination, and that the 1.5145-eV line is the (D^+,X) emission with the sensitive temperature dependence arising from dissociation of (D^+,X) into a free hole and neutral donor. This alternative is eliminated because the 1.5133-eV line is left without explanation; it is not energetically possible to assign it to (D^0,h) [i.e., $E_{X_{D^+}}$ must exceed E_{D^0} in order for (D^+,X) to be stable]. In addition, a weak shoulder is sometimes discernible at 1.5150 eV just above the (D^0,X) line. This might be attributed to $j\text{-}j$ splitting of the energy levels of the (D^0,X) system. Such a splitting is expected and observed in other materials for multiparticle complexes.[24] Since the doublet structure is not a prominent feature of our spectra, we have not stressed its presence.

The temperature dependence of the 1.5133-eV emission line is consistent with a single thermal dissociation (or ionization) process characterized by an activation energy approximately equal to the donor ionization energy of 6.8 meV; this leads to the suggestion that the 1.5133-eV line arises from (D^0,h) transitions. However, assignment of this line to the (D^+,X) complex cannot be completely ruled out. Since previous reports[8,10,1] refer to exciton complexes, we have maintained the

[23] P. J. Dean, J. C. Tsang, and P. T. Landsberg, Bull. Am. Phys. Soc. **13**, 404 (1968).

[24] P. J. Dean, W. F. Flood, and G. Kaminsky, Phys. Rev. **163**, 721 (1967).

latter notation. It is interesting to consider the rates for a neutral donor capturing a hole to form (D^+,X), which can subsequently radiatively annihilate, and the radiative annihilation rate of an electron trapped on a donor ion (D^0) with a free hole, $R_{D\text{-}B}$. The radiative recombination rate increases as the third power of effective radius, $R_{D\text{-}B} \sim a^{*3}$. The capture rate w_{cap} is more difficult to estimate.[25] Large diffuse impurities are readily polarized by a free carrier, so intuitively we can argue that w_{cap} would increase very rapidly with a^*, indicating that (D^+,X) formation should dominate (D^0,h) radiative recombination. This conclusion does not support our contention that 1.5133-eV line is (D^0,h) recombination. Additional work is needed to remove the ambiguity.

The emission line at 1.5125 eV does not appear in all samples. If it does appear, it is always weak in n-type material. It emerges as a stronger line in p-type material, though it remains weaker than the $\sim$1.49-eV "acceptor lines." This behavior of the 1.5125-eV line together with its energy position is consistent with its assignment to the exciton–neutral-acceptor (A^0,X) emission. It is ruled out as a different trace impurity (or donor emission line) by its consistent increase in going from n- to p-type material and its correlation with the band-acceptor (A^0,e) 1.4926-eV emission. Both the (A^0,X) and (A^0,e) appear to vary proportionally with the number of neutral acceptors [neglecting the low-temperature changes in (A^0,e) due to Auger ionization of the (D^0,X) system]. However, since the (A^0,X) emission is often weak or absent, it is difficult to investigate carefully.

In conclusion, the assignments of the free-exciton, (D^0,X), $(B\text{-}A)$, and $(D\text{-}A)$ emission lines are regarded as fairly reliable. Identification of the (D^+,X), (A^0,X), and (A^-,X) emissions is based in part on elimination of other possibilities by the assignments regarded as reliable. The dominant impurity in epitaxial GaAs grown in SiO_2 reactors is Si. The principal tools used herein for studying the photoluminescence spectra are temperature dependence, variations with changes in impurity concentration, and the relative energy positions predicted from theory. Since the expected energy positions cannot be considered quantitatively reliable, the dependence on temperature and impurity concentration is necessary to establish the assignments unambiguously. Other techniques such as magnetic or pressure experiments could provide additional evidence to remove the remaining uncertainties.

Last, observation of the exciton lines, both bound and free, is a consequence of the improved quality of epitaxial GaAs. As the impurity content increases, the exciton lines tend to become increasingly difficult to see, and the $(D\text{-}A)$ emission emerges as the only important emission. Apparently the important radiative emission mechanisms in high-purity, epitaxial GaAs and impure epitaxial or bulk-grown GaAs are completely different.

[25] M. Lax, Phys. Rev. **119**, 1502 (1960).

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