Free-Carrier and Exciton Recombination Radiation in GaAs

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Photoluminescence studies were made at liquid-helium temperatures of epitaxial GaAs with ionized-impurity concentrations $\lesssim 10^{15}$ cm^{-3}. Narrow linewidths at half-height were achieved by using material of high purity and perfection, by using low intensities of illumination, and by observing excitons bound to impurities which are almost entirely in one state of ionization. Impurity-exciton lines were ≈ 0.1 meV wide at 4.2°K, free-exciton lines ≈ 1 meV wide for $T \leq 4.2$°K, and free-charge-carrier (band-gap) radiation $\lesssim 0.24$ meV wide at 1.4°K. Free-carrier recombination radiation at 1.4°K establishes the band gap E_G at 1.5202 eV ± 0.3 meV. The exciton binding energy G from the $n=1$ exciton was found to be $G(1)=4.7\pm 0.4$ meV, and from the $n=2$ exciton to be $G(2)=3.6\pm 0.6$ meV. The $G(1)$ value agrees with that given by Wright and Galeener, and the $G(2)$ value with that given by Sturge for $G(\infty)$. An ionized Zn-exciton complex has been observed, as recently predicted by Sharma and Rodriguez. Lines from excitons bound at ionized and neutral Zn and at ionized Se are, respectively, 31.2 ± 0.4, 8.0 ± 0.3, and 6.1 ± 0.3 meV below E_G. The free-exciton and impurity-exciton binding energies are satisfied by $m_h^*/m_e^* \approx 5$, with impurity ionization energies of ≈ 26 meV for Zn and ≈ 6 meV for Se. The neutral Zn-exciton line and the ionized Se-exciton line have been resolved, respectively, as a triplet and doublet with separations ≈ 0.2 meV and widths ≈ 0.1 meV. This structure arises from exchange splitting of the states formed from the electrons and holes by j-j coupling. Two lines arising from the excited state of the neutral Zn-exciton complex are identified at ± 6 meV from the ground state. The ionized Zn-exciton complex is accompanied by an illumination-dependent phonon wing probably associated with a resonant vibration.

INTRODUCTION

LOW-TEMPERATURE (4.2 to 1.4°K) photoluminescence studies[1] of relatively pure (10^{14} to 10^{15} cm^{-3} impurities) epitaxial GaAs, grown by Williams, have revealed several new features. Radiation from recombination of free carriers and of free excitons provides the first direct measurement of the gap and the $n=1$ and 2 energy levels of the free exciton. Sharp lines have been observed which result from recombination of excitons bound to neutral and ionized Zn acceptors and to ionized Se donors. The existence of an ionized acceptor-exciton complex for the exciton hole-to-electron mass ratio m_h^*/m_e^* which we find for GaAs was predicted only recently by Sharma and Rodriguez.[2] A new effect has been found in the variation with intensity of illumination of the width of the phonon wing on the low-energy side of the ionized Zn-exciton line. Higher resolution than previously employed reveals the exchange splittings of j-j coupled states in two bound complexes.

In studies of the optical absorption of GaAs as a function of temperature and photon energy, Sturge[3] established the energy gap $E_G=1.521\pm 0.0015$ eV at $T \leq 21$°K. For the binding energy G of the free exciton, Sturge obtained $G=3.4\pm 0.2$ meV from the slope of the absorption coefficient in the exciton continuum ($n=\infty$) region, utilizing the theory of Elliott.[4] We designate Sturge's G as $G(\infty)$. Wright and Galeener[5] deduced $G(1)\approx 5$ meV from photoluminescence in a high magnetic field.

An estimate of $G(1)$, which allows for the degeneracy of the light- and heavy-hole bands, is obtained from the theoretical $n=1$ direct exciton binding energy in Ge; this estimate gives $G(1)=4.4$ meV in GaAs.[3,6] Wright[7] has estimated $G=5.25$ meV. Since the corresponding exciton rotation frequency, $\omega \approx 2\times 10^{13}$ sec^{-1}, approaches the reststrahl frequency $\approx 5\times 10^{13}$ sec^{-1} in GaAs,[8,9] $G(1)$ will be greater[10,11] than the above estimate which used the static dielectric constant ϵ_0 and should correspond to a value employing ϵ between ϵ_0 and ϵ_∞, although probably closer to ϵ_0. However, ϵ_0 does apply to exciton binding energies for $n \geq 2$. For example, in Cu_2O,[11] $G(1)$ is 45% greater than $G(2, 3, \cdots, 10)$. Further, in GaAs, because of the degeneracy of the light- and heavy-hole bands, excitons of different n can correspond to different mixtures of light and heavy holes in the exciton-hole mass m_h^*. For these reasons explicit measurements are needed of the exciton energy levels relative to E_G.

Impurity-exciton binding energies as functions of m_h^*/m_e^* have been calculated by Kohn,[12] Munschy,[13]

[1] M. A. Gilleo, D. E. Hill, and F. V. Williams, Bull. Am. Phys. Soc. **12**, 656 (1967); P. T. Bailey, M. A. Gilleo, and D. E. Hill, *ibid.* **13**, 497 (1968); M. A. Gilleo, P. T. Bailey, and D. E. Hill, *ibid.* **13**, 497 (1968).
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[6] J. O. Dimmock, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1967), Vol. 3, p. 314. G for GaAs should read 4.1 meV, not 5.1 meV; Dimmock took $\epsilon_0=13.5$, $m_e^*=0.084$.
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TABLE I. Electrical properties of epitaxial GaAs used in experiments; all substrates are of (100) orientation.

Sample No.	T (°K)	Charge carrier type and concentration (cm^{-3})	μ (cm^2/V sec)	N_I (cm^{-3})	n/N_I	Dopants added
619928-6[a]	77	$n=1.1\times10^{14}$	53 000	5.5×10^{14}	0.2	None[e]
619940-5[b]	300	...[d] ...	...	...	...	None[e]
619953-5[b]	77	$n=3.0\times10^{15}$	30 000	4×10^{15}	0.75	Se
629803-1[b]	300	$p=1.5\times10^{14}$	420	...	...	Zn, Se
629803-2[b]	300	$p=1.4\times10^{14}$	410	...	...	Zn, Se
629803-3[b]	300	p	(between 629803-1 and 629803-2)			Zn, Se
629849-1[c]	77	$n=4.4\times10^{14}$	28 900	3×10^{15}	0.15	Zn, S

[a] Substrate doped n-type with about 10^{18} cm^{-3} Sn.
[b] Substrate doped n-type with about 10^{18} cm^{-3} Si.
[c] Substrate doped with Cr to give high resistivity.
[d] Resistivity was too high to permit measurements.
[e] No dopant was deliberately added, but this run followed a Se-doped run so that Se may be present.

and Sharma and Rodriguez,[14] for excitons bound to single, neutral donors and acceptors, and by Hopfield,[15] and Sharma and Rodriguez,[2] for excitons bound to single, ionized donors and acceptors. While neutral impurity-exciton complexes exist for all values of m_h^*/m_e^*, ionized impurity-exciton complexes exist only for certain ranges of m_h^*/m_e^*. The predicted existence of an ionized acceptor-exciton complex[2] for $m_h^*/m_e^* \gtrsim 3$ is important for GaAs.

For each bound state in a material such as GaAs the mass ratio m_h^*/m_e^* will correspond to a different mixture of light and heavy holes. Nonetheless, similar values of m_h^*/m_e^* should apply to the $n=1$ exciton and shallow impurity-exciton states. For deeper impurity-exciton states (e.g., ionized acceptor-exciton states) central cell corrections will also affect m_h^*/m_e^*.[15]

The photoluminescence work of Nathan and Burns at ≥ 4°K,[16] and of Benoit à la Guillaume and Tric at 20°K,[17] has shown evidence for bound and free excitons in GaAs. Identification of the impurity-exciton complexes was not made nor was band-gap or free-exciton radiation for $n>1$ observed. In more recent work by Williams *et al.* at ≥ 20°K,[18] the radiation associated with specific impurities, mostly acceptors, has been identified. However, the mechanism by which it is produced was not clearly identified.

We now have available GaAs of high purity and perfection. With a great reduction in radiation associated with impurities it becomes possible to detect the radiation from free-exciton and free-carrier recombination. Even so it is difficult, for several reasons, to observe radiation from states with energies near E_G. First, the radiation from the higher-lying levels is seriously reduced in photoluminescence at liquid-helium temperatures by the factor $\exp(-h\nu/kT)$ from the Bose sattistics. Also Elliott[4] has shown that the oscillator strengths of exciton transitions have n^{-3} dependence. The dissociation energies of excitons in GaAs, which are approximately $3.4/n^2$ meV for $n\geq 2$, decrease so rapidly that the populations of excitons with $n>2$ will be very small at liquid-helium temperatures and above. The $n=2$ exciton and E_G lines are clearly discernible only at the lowest temperature and illuminating intensity employed. At higher temperature or illumination these two lines vanish into additional radiation which is increasing steeply toward the peaks of the $n=1$ exciton and impurity-exciton lines, which are stronger than the $n=2$ exciton and E_G lines by 10^2 to 10^3 times. The broadening of these stronger lines by increase in temperature and/or illumination increases the height of their skirts near E_G (this effect is especially evident for the lines arising from the ionized Se-exciton complex). At still higher illuminations shielding effects arising from photo-produced charge carriers will quench[7,19,20] in turn the E_G, $n=2$, $n=1$ and even the shallow impurity-exciton lines. For the above reasons it is not surprising that the $n=2$ exciton and E_G lines have not previously been seen.

Our experimental results confirm the results of Sturge[3] and Wright and Galeener,[5] and establish $G(1)$ and E_G with higher precision. Definite information was also obtained concerning the existence of exciton-impurity complexes, whence ionization energies for the impurities were inferred from theory.

EXPERIMENTAL

Material

The epitaxial GaAs used in these experiments was grown by Williams of these Laboratories. Zn, Se, and S impurities were introduced during growth by the halide transport method. The donor concentration N_D, acceptor concentration N_A, the total ionized-impurity concentration N_I, and the electron or hole concentration n or p were determined from the Hall constant and mobility data. Samples grown on (100) orientation with $N_I \lesssim 10^{15}$ cm^{-3} gave the best results (Table I). In the case of a (100) specimen with high resistivity at room

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[15] J. J. Hopfield, in *Physics of Semiconductors*, edited by M. Hulin (Academic Press Inc., New York, 1964), pp. 725–735.
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temperature N_I was inferred: Impurity concentrations in (111)B samples differ from those in (100) samples made in the same run by multiples[21] of 6.3 for Se and 0.43 for Zn.

Apparatus

The photoluminescence measurements were carried out with the sample immersed in liquid helium. The vapor pressure was reduced to achieve temperatures down to about 1.4°K. The spectra were detected by an RCA C70102B photomultiplier with an S1 surface at solid CO_2 temperature. A Jarrell-Ash Model 84-110 grating monochromator dispersed the radiation. The grating has a dispersion of $\frac{1}{16}$ mm/Å in second order.

A dichroic mirror of the long-wavelength-pass type with 50% transmission at 6000 Å was used in conjunction with a Schott RG-10 filter in the monochromator beam. A $CuSO_4$ solution and two Schott KG-3 filters were in the beam of the 500-W Hg arc which was reflected to the sample by the dichroic mirror. These filters reduced to a negligible value the radiation which reached the detector from the arc. Neutral-density filters were used for large attenuation and screens for smaller, incremental attenuation of the exciting radiation. For work in the region of the $n=2$ exciton and E_G lines an O. D. 1 neutral filter was often replaced, with good results, by a Corning 4-64 green filter. In these experiments, as in most photoluminescence studies, the exciting photons have energies considerably greater than E_G.

The recorded data were obtained in terms of relative response per wavelength interval. Calibration of the system in terms of relative number of photons per wavelength interval per sec was carried out with a calibrated tungsten lamp. The data read from the strip chart were processed by computer to yield a plot in terms of relative number of photons per energy interval per sec. The computer program contained corrections for monochromator wavelength error, the index of refraction of air, any additional filter used with the monochromator, and, in some cases, background corrections.

BASES OF IDENTIFICATIONS

Free-carrier and free-exciton recombination lines should be independent of the impurities present, and thus common to all GaAs, whether n, p, or high-resistivity type material. Other lines whose occurrence and character vary with impurity and conductivity type can then be identified with the impurities and their ionization states.

The characteristic linewidths are used to aid in identifying the lines with their different origins. Recombination of bound, immobile excitons yields half-widths which are usually $<kT$.[22,23] The free-carrier recombination line for the allowed $\Gamma_6 \rightarrow \Gamma_8$ transition in GaAs has the form $\exp[-(h\nu-E_G)/kT]$ for $h\nu \geq E_G$ and $\gg kT$, and zero for $h\nu<E_G$.[16,24] This applies for $h\nu-E_G \lesssim G$, and follows from the step-function form of the free-carrier absorption coefficient α at E_G,[4] which is multiplied by the Planck coefficient to obtain the radiation spectrum via the detailed balance principle. The half-width of this line is $\approx 0.7kT$. At helium temperatures a direct free-exciton line has a temperature-independent half-width Γ_i, which depends on encounters between excitons and imperfections such as a surface or impurity.[25–27] In CdS $\Gamma_i \approx 1$ to 3 meV,[25–27] or $>kT$ for $T \lesssim 4.2$°K. At low temperatures in GaAs, Sturge[3] observed a Gaussian free-exciton absorption line of temperature-independent width ≈ 3 meV, which corresponds to a width at half-maximum of $\Gamma_i \approx 7$ meV.

The energies obtained by Sturge[3] and by Wright and Galeener[5] are used as further aids to identification of the free-carrier and free-exciton lines. Sturge obtained $E_G = 1.521 \pm 0.0015$ eV and $G(\infty) = 3.4 \pm 0.2$ meV. Hence the $n=2$ line should lie ≈ 0.85 meV below E_G. Wright and Galeener obtained $G(1) \approx 5$ meV.

The impurity-exciton complexes can be identified with specific impurities by examining (i) variations of line strengths with doping, (ii) extents of agreement between observed and theoretical[2,12–15] binding energies, (iii) changes of linewidths with conductivity type, and (iv) effects of exchange splittings.

RESULTS

Free Carriers and Free Excitons

In n-type [Fig. 1(a)], p-type [Fig. 1(b)], and high-resistivity material [Fig. 1(c)], lines which yield $E_G = 1.5202 \pm 0.3$ meV, $G(2) = 3.6 \pm 0.6$ meV, and $G(1) = 4.7 \pm 0.4$ meV satisfy the criteria just enunciated for identifying free-carrier and free-exciton recombination radiation. Our observed values for E_G and $G(2)$ agree with Sturge's E_G and $G(\infty)$, and our $G(1)$ with Wright and Galeener's $G(1)$.

The width of the E_G line was determined mainly by slit width in all cases. At 1.38°K a half-width of 0.24 meV was observed with a slit width of 0.15 meV, the smallest slit width which could be used with so weak a signal. Its theoretical shape has a half-width $\lesssim 0.1$ meV at 1.38°K. At somewhat higher temperatures the E_G line was not observable, for the reason given earlier. Confusion of the line designated as E_G with the $n=3$ exciton line seems unlikely. The $n=3$ line should be much weaker than the $n=2$ line because of the n^{-3} dependence of exciton oscillator strengths,[4] because of

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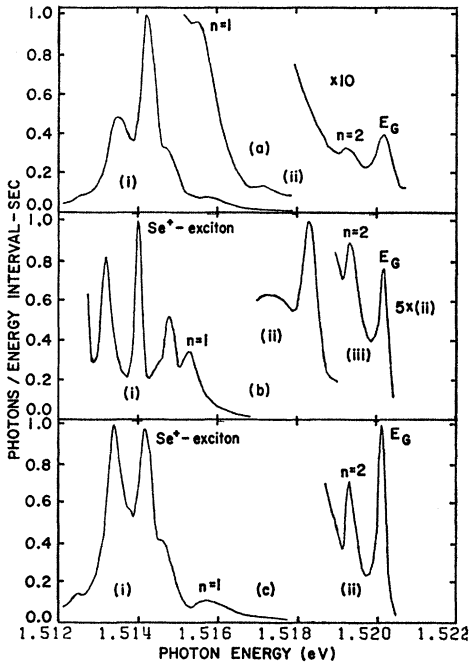

FIG. 1. Free-carrier, free-exciton, and impurity-exciton photoluminescence of GaAs: (a) n-type (619928-6), spectra at (i) 2.08°K with 0.18-meV resolution, (ii) 1.38°K with 0.3-meV resolution; (b) p-type (629803-3), spectra at (i) 4.2°K with 0.15-meV resolution, (ii) 1.46°K with 0.3-meV resolution, (iii) 1.36°K with 0.21-meV resolution; (c) high-resistivity (619940-5), spectra at (i) 2.12°K with 0.09-meV resolution, and (ii) 1.38°K with 0.15-meV resolution.

the Planck function, and because of thermal dissociations. But the observed line is stronger than the $n=2$ line. The E_G line, on the other hand, arises from the continuum of unbound exciton states (free charge carriers) with a constant absorption coefficient for $0\leq(h\nu-E_G)\lesssim G$.

The allowed $n=1$ free-exciton line has an almost

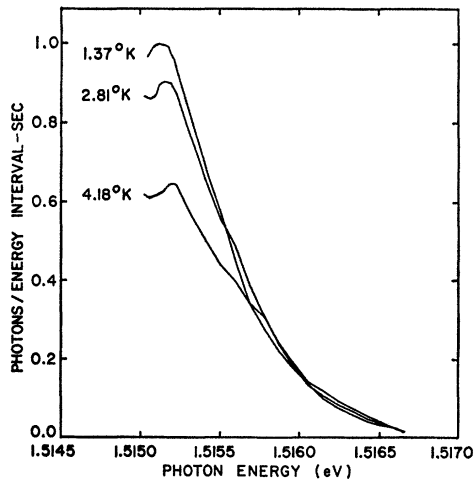

FIG. 2. Temperature dependence at constant illumination of $n=1$ free-exciton photoluminescence of p-type GaAs (629803-3). Spectra at 1.37°, 2.81°, and 4.18°K with 0.07-meV resolution.

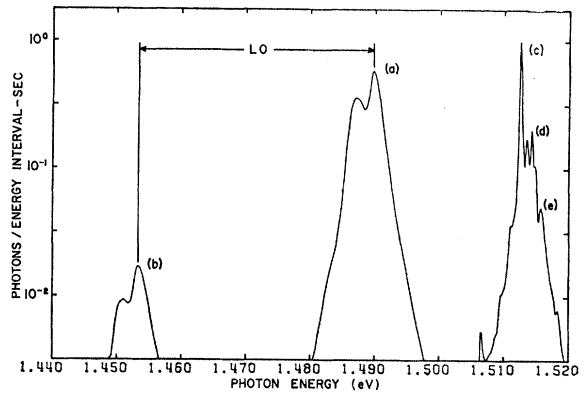

FIG. 3. Photoluminescence spectrum of Zn and Se-doped, p-type GaAs (629803-1) at 4.2°K, with resolution 0.14 meV down to 1.480 eV and 0.3 meV at lower photon energies. (a) Zn^--exciton line, (b) its LO phonon replica, (c) Zn^0-exciton line, (d) Se^+-exciton line, (e) $n=1$ free-exciton line.

temperature-independent half-width $\Gamma_i\approx1$ meV (Fig. 2), which is $>kT$ for $T\leq4.2$°K. The strength of the line increases little with decreasing T, probably because $G(1)/kT\approx13$ at 4.2°K, so that thermal ionization is negligible. The difference between Sturge's $\Gamma_i\approx7$ meV and our $\Gamma_i\approx1$ meV is believed to be due to strains in Sturge's specimens[3] and to his impurity concentrations, $N_I\approx3\times10^{16}$ to 3×10^{17} cm^{-3}, which exceed the concentrations $N_I\lesssim10^{15}$ cm^{-3} in our GaAs. The $n=2$ exciton line, which is observed only at 1.4°K, has a width of $2kT$ to $3kT$ in the best-resolved case [Fig. 1(c)].

The $n=1$ exciton peak appears to shift a few tenths of an meV toward higher energy as the room-temperature conductivity-type changes from p to n, i.e., as N_A-N_D changes from positive to negative. This apparent shift may result from the intrusion, on the low-energy side of the $n=1$ peak, of radiation associated with neutral donors which may or may not have excitons bound to them. This intruding radiation (Fig. 1) has not been clearly resolved. The uncertainty range, 0.8 meV, of our observed $G(1)$ arises from this apparent shift of the $n=1$ peak, and from our inability to resolve the low-energy side of the peak. The large uncertainty range, 1.2 meV, of $G(2)$ is four times the uncertainty of the separation of the $n=2$ exciton line from the E_G line.

In addition to the uncertainties just mentioned, there is uncertainty[10,11] of the value of ϵ which applies to $G(1)$ and to the impurity-exciton binding energies: ϵ is between $\epsilon_0\approx13$ and $\epsilon_\infty\approx11$,[28] but probably closer to ϵ_0. For $12\lesssim\epsilon\lesssim13$ and electron effective mass $m_e^*=(0.066\pm0.002)m_e$[29] the observed free-exciton and impurity-exciton binding energies are satisfied by $3\lesssim m_h^*/m_e^*\lesssim7$. Thus m_h^* is between the light- and heavy-

[28] Several slightly differing values of ϵ_0 and of ϵ_∞ have appeared. See Ref. 8; K. G. Hambleton, C. Hilsum and B. R. Holeman, Proc. Phys. Soc. 77, 1147 (1961); several letters in Appl. Phys. Letters 11, No. 11 (1967).

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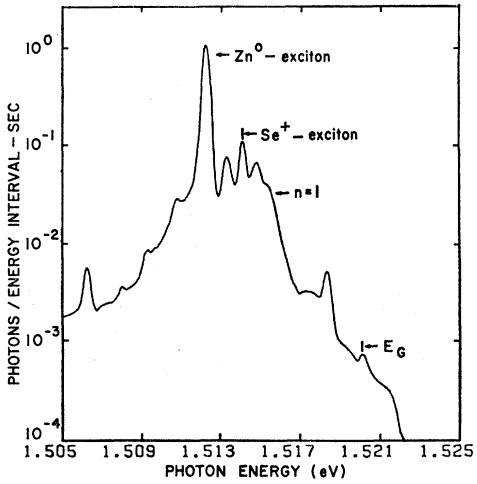

FIG 4. Photoluminescence spectrum of Zn- and Se-doped, p-type GaAs (629803-3) at 1.46°K with 0.3-meV resolution. The satelite lines at ±6 meV from the Zn^0-exciton line are prominent.

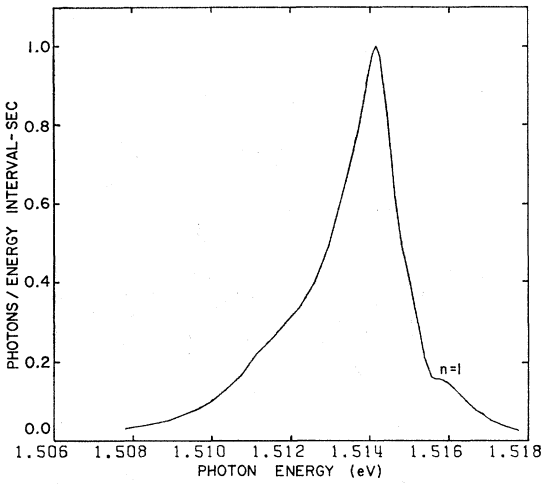

FIG. 5. Photoluminescence near 1.514 eV of Se-doped, n-type GaAs (619953-5) at 4.2°K with 0.15-meV resolution.

hole masses $0.1m_e$ and $0.6m_e$. In the discussions which follow we use $m_h^*/m_e^* \approx 5$.

An effort was made to observe the linear Stark effect for the $n=2$ exciton line, which should show a 1-meV splitting in a field ≈ 150 Vcm^{-1}. However, photoconductivity seriously reduces fields in the illuminated region; no field effects were observed for field strengths of up to 10^5 Vcm^{-1} applied to the surface.

Impurity-Exciton Complexes

For single impurity-exciton complexes the photoluminescence spectrum of interest extends from about 1.44 to 1.52 eV (Fig. 3). The greatest detail is observed in the range 1.505 to 1.519 eV (Fig. 4).

Donor-Exciton Complex

The ionized Se-exciton line, at 1.5141 eV [Fig. 1(b)], was identified from its intensity variation with Se concentration and with conductivity type, by using intensity comparisons with the $n=1$ exciton line and between samples. The binding energy of the Se^+-exciton complex is 6.1±0.3 meV, or 1.4 meV relative to $G(1)$. For a donor ionization energy $E_D \approx 13.6 m_e^*/\epsilon^2$ eV$\approx$6 meV, the binding energy relative to $G(1)$ is about $0.2E_D$, in agreement with estimates of such binding[2,15] for $m_h^*/m_e^* \approx 5$.

The Se^+-exciton line is narrowest and weak in a p-type sample [Fig. 1(b)]. In n-type GaAs the strength of the Se^+-exciton line increases with N_D (Fig. 5), but the line also broadens. With $N_D \gtrsim 10^{15}$ cm^{-3} the Se^+-exciton peak dominates the spectrum; the $n=1$ exciton line can no longer clearly be distinguished. Higher illuminating intensities also cause the lines in this region to broaden until separations are indistinguishable.

Under high resolution (0.05 meV) and with weak illumination (4-64 filter), the 1.1541-eV line is found to be a doublet (Fig. 6). This structure arises from the exchange splitting[30] of the states $J=2$, 1 of the bound complex consisting of a hole ($j=\frac{3}{2}$), an electron ($j=\frac{1}{2}$), and a Se^+ impurity ($j=0$). An exciton recombination transition to the impurity ground state is allowed for the $J=1$ state (higher in energy) and forbidden for the $J=2$ state, so the $J=2$ line should be narrower. This situation was first discussed for an oxygen-exciton complex in ZnTe[31] and for a nitrogen-exciton complex in GaP[32] (the oxygen and nitrogen in each case being isoelectronic acceptors). For the Se^+-exciton complex the lower line (Fig. 6) has a half-width of about 0.1 meV,

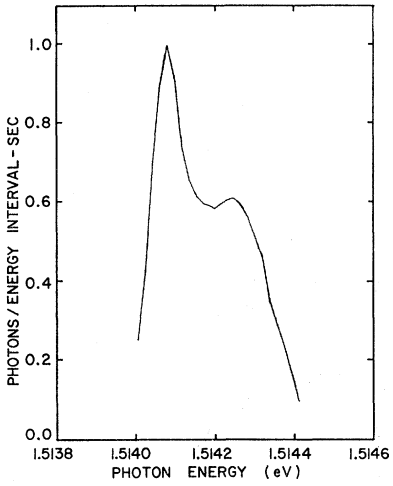

FIG. 6. Fine structure of Se^+-exciton line showing exchange split $J=2$ (lower, forbidden) and $J=1$ states. Photoluminescence of Zn and Se-doped, p-type GaAs (629803-3) at 4.18°K with 0.05-meV resolution.

[30] Suggested to us by P. J. Dean.

[31] R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters 8, 391 (1962); J. J. Hopfield, D. G. Thomas, and R. T. Lynch, *ibid.* **17**, 312 (1966).

[32] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963); D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Letters **15**, 857 (1965).

and the higher a half-width of about 0.2 meV; the separation is about 0.15 meV.

The Se^+-exciton line is narrowest in p-type material because in this case Se^+ is the only stable state for the Se donor impurity. In n-type material the donors are ionized only a part of the time, which produces lifetime broadening; some delocalization of the electrons[33] may also contribute to broadening. Se^0-exciton radiation might intrude in n-type material but has not been identified.

Two broader lines (half-widths ≈ 0.4 meV at 4.2°K) are located symmetrically about the sharp 1.5141-eV line with peaks at ± 0.78 meV and shoulders at $\approx \pm 0.4$ meV [Fig. 1(b)]. These two lines appear to be associated with the 1.5141-eV line, but the association is not understood. A weak LO phonon replica of the 1.5141-eV line occurs at about 1.478 eV [Fig. 7(a)].

Acceptor-Exciton Complexes

Identification of the ionized Zn-exciton complex was made by observing its appearance with Zn doping. The neutral Zn-exciton complex was identified by noting that it disappeared in n-type, Zn-doped material. The ionization energy for Zn in GaAs deduced from the binding energies of these complexes is consistent with the value obtained from electrical measurements. In addition the line associated with the Zn^0-exciton complex was resolved as a triplet, which is expected for this state from exchange splitting.[30]

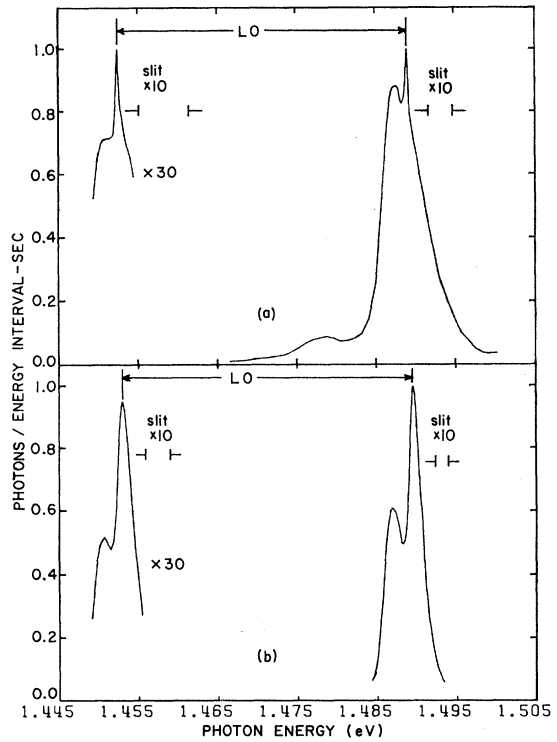

FIG. 7. The Zn^--exciton line, its phonon wing, and their LO phonon replicas. Photoluminescence of (a) S and Zn-doped, n-type GaAs (629849-1) at 4.2°K, with 0.3-meV resolution at 1.490 eV and 0.6-meV resolution at 1.454 meV; (b) Zn and Se-doped, p-type GaAs (629803-1) at 4.2°K, with 0.15-meV resolution at 1.490 eV and 0.30-meV resolution at 1.454 meV.

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

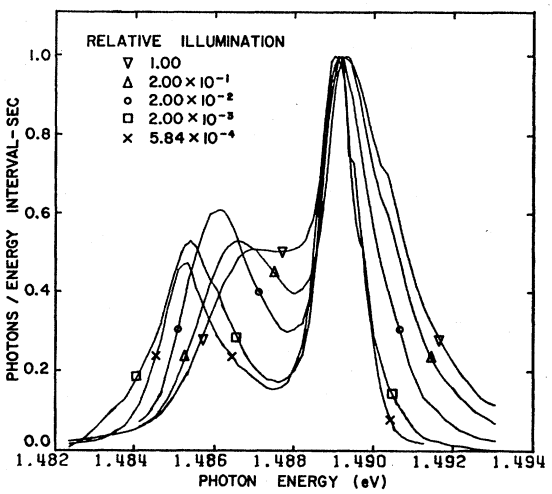

FIG. 8. Variation with intensity of illumination of the phonon-wing relative to the no-phonon Zn^--exciton line (normalized to unity). Photoluminescence of Zn and Se-doped, p-type GaAs (629803-3) at 4.2°K with 0.3-meV resolution.

The line at 1.4890 eV (Fig. 7) is identified with excitons bound at Zn^- acceptors (binding energy 31.2 ± 0.4 meV). An assumption of $m_h^*/m_e^* \approx 5$, for which ratio the binding energy relative to E_G is $\approx 1.2E_A$,[2] yields an acceptor ionization energy $E_A \approx 26$ meV. This agrees with the value obtained from the data of Ermanis and Wolfstirn[34] when their data are linearly extrapolated to low acceptor concentration. This line is sharp [Fig. 7(a)] (half-width at 1.4°K $\approx$ slit width of 0.3 meV) in n-type GaAs in which only ionized acceptors are present. In p-type material the line is wider [Fig. (7b)] (half-width ≈ 1 meV at 4.2°K) because the acceptors are neutral for $kT \ll E_A$ except those ionized by donor impurities, so that lifetime broadening results (as for the Se^+-exciton line in n-type material). Because this line is weak in the n-type specimens which were used, fine structure, if present, could not be resolved.

A phonon wing occurs on the low-energy side of the 1.489-eV line, and the ratio of the intensity of the wing peak to the no-phonon peak is, respectively, about 0.5 and 0.9 in p- and n-type, Zn-doped specimens, even though the line is much stronger in the p-type specimens. In separate reports[35,36] the phonon wing on the 2.536-eV line in CdS has exhibited different relative heights at 4.2°K, which may be due to different impurity contents of the specimens, as in our data for GaAs.

[31] F. Ermanis and K. Wolfstirn, J. Appl. Phys. **37**, 1963 (1966).

[35] J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1962), pp. 75–80.

[36] E. F. Gross, B. S. Razbirin, and S. A. Permogorov, Dokl. Akad. Nauk SSSR **147**, 338 (1962) [English transl.: Soviet Phys.—Dokl. **7**, 1011 (1963)]; E. F. Gross, S. A. Permogorov, and B. S. Razbirin, *ibid.* **154**, 1306 (1964) [English transl.: *ibid.* **9**, 164 (1964)].

The no-phonon line and phonon wing are accurately replicated (Fig. 7) at energies lower by 36.4±0.2 meV, the $\mathbf{k}=0$ LO phonon energy.[9] The peak position of the wing relative to the no-phonon line varies with the intensity of illumination (Fig. 8) from ≈ -4 meV to ≈ -2 meV for an increase in illuminating intensity of $\approx 2\times 10^3$ times. Simultaneously, the no-phonon line moves ≈ 0.4 meV towards higher energy. These effects may arise from an increase in electrostatic shielding with free-carrier concentration. The relative intensity of the wing increases with decreasing temperature (4.2 to 1.5°K) (Fig. 9).

In Zn-doped, p-type specimens the line at 1.5122 eV (Fig. 4) is identified with excitons bound at Zn^0 acceptors. For $m_h^*/m_e^* \approx 5$ the binding energy predicted by Kohn[12] and by Munschy[13] is $\approx 0.2E_A$ relative to E_G, or ≈ 5 meV for $E_A \approx 26$ meV. This is somewhat smaller than the observed energy 8.0±0.3 meV. Sharma and Rodriguez[14] computed the binding only for $0 \leq m_h^*/m_e^* \leq 1$. However, their curve for this region differs significantly from those of Kohn and Munschy, and suggests binding energies up to 50 to 100% larger for $1 < m_h^*/m_e^* < 10$.

The Zn^0-exciton line has been resolved into three components (Fig. 10) at 1.51208, 1.51222, and 1.51239 eV (relative precision ±0.03 meV), with half-widths ≈ 0.1 meV and intensities roughly in the ratio 1:2:1, all at 4.2°K. Such a triplet arises from the exchange splittings of the j-j coupled states of two identical p-like holes ($j=\frac{3}{2}$), giving $J=2$ (lower) or 0 (as in atomic Po), and of an s-like electron ($j=\frac{1}{2}$), giving $J=\frac{5}{2}$ (lowest), $\frac{3}{2}$, $\frac{1}{2}$. All of these states have allowed transitions to the Zn^0 ground state ($j=\frac{3}{2}$) so the three lines should have similar widths. A small peak at 1.5126 eV is observed in other material not containing Zn^0 [Fig. 1(c)] and is not associated with the triplet. An analogous triplet has recently been discussed for the case of Si.[37]

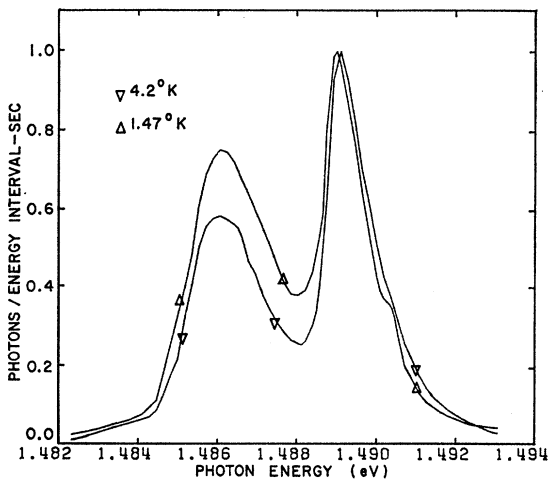

FIG. 9. Variation with temperature of the phonon-wing relative to the no-phonon Zn^--exciton line (normalized to unity). Photoluminescence of Zn and Se-doped, p-type GaAs (629803-3) with 0.14-meV resolution.

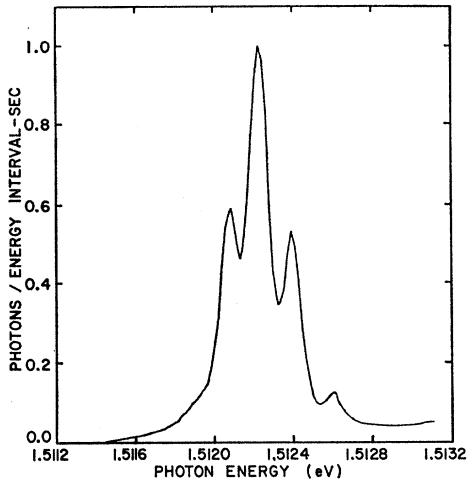

FIG. 10. Fine structure of Zn^0-exciton line showing exchange split $J=\frac{5}{2}$ (lowest), $\frac{3}{2}$, $\frac{1}{2}$ states. Photoluminescence of Zn and Se-doped, p-type GaAs (629803-3) at 4.2°K with 0.04-meV resolution.

Two lines clearly associated with the Zn^0-exciton line are located symmetrically about it at energy displacements of ±(6.0±0.1) meV (Fig. 4). The higher-energy line is identified with the first excited state of the Zn^0-exciton complex,[38] the lower with a second-order transition from the ground state (central line), through the excited state, with emission of an energy-conserving acoustic phonon. Such a second-order transition through an excited state of a bound-exciton complex has been observed in ZnTe.[31] The 6-meV phonon has a wavelength ≈80 Å (LA), or ≈40 Å (TA)[8], which is less than the size of the complex (≈100 Å). This accounts for the comparative weakness, considering the Planck factor, of the lower line. An estimate of the first excitation energy of this complex can be deduced from the analysis of Kohn.[12] In this analysis the dissociation energy of the complex is $E_{\ominus++-} = E_{\ominus++(-)} + E_{\ominus+(+)} - G$, where $E_{\ominus++(-)}$ is the energy required for removal of the electron, $E_{\ominus+(+)}$ for the subsequent removal of a hole, and G is the energy gained by recombining the freed electron and hole as an exciton. We know that $E_{\ominus++-} = 8.0$ meV, $E_{\ominus+(+)} = 0.055E_A \approx 1.7$ meV, and $G=4.7$ meV, so we deduce $E_{\ominus++(-)} \approx 6.3$ meV. By assuming that the first excitation energy of the complex lies between $\frac{3}{4}$ of the binding energy of the last particle to be bound and $\frac{3}{4}$ of the ionization energy of the entire complex we find an excitation energy between 4.7 and 6.0 meV, in fair agreement with the observed energy 6.0 meV. The same procedure applied to first and second excited states of a Se^0-exciton complex in GaP gives energies of $\frac{3}{4}$ and $\frac{8}{9}$ times 25.5 meV, i.e., 19.1 and 22.6 meV, or $\frac{3}{4}$ and $\frac{8}{9}$ times 30.6 meV, i.e., 22.9 and 27.2 meV, which approximate the observed energies 16.1 and 22.5 meV.[39]

[37] P. J. Dean, W. F. Flood, and G. Kaminsky, Phys. Rev. **163**, 721 (1967).
[38] Suggested to us by R. A. Faulkner.
[39] P. J. Dean, Phys. Rev. **157**, 655 (1967).

DISCUSSION

The results presented for photoluminescence in the region up to 7 meV below E_G were found to be obtainable only with as low an intensity of illumination as the sensitivity of the apparatus permitted. The photon flux in the beam used to excite photoluminescence in this region is estimated to be of the order of 10^{16} photons sec^{-1}. At flux densities higher by as little as two times, good resolution could not be achieved.

For the Zn^--exciton complex the effect of increasing illumination intensity is a reduction of the separation of the phonon wing from the no-phonon line and a shift of the latter to higher energy by a fraction of an meV. The phonon wing shift toward higher energy is not consistent with the model of Duke and Mahan[40] which involves crystal phonon modes. The phonon wing probably arises from a resonant vibration of Zn, as for Cd acceptors in GaP.[41] In this case shielding would reduce the resonant frequency. Shielding would also reduce the ionization energy of Zn and account for the shift of the no-phonon line at 1.489 eV.

A band near 1.490 eV (half-width $\approx$10 meV at 2°K), with a phonon replica near 1.455 eV, has been observed by Leite and DiGiovanni[42] and attributed to donor-acceptor-pair recombination. Very low impurity concentrations exclude our observation of similar recombination. A band of position and width similar to that of Ref. 42 has also been regarded as free-electron recombination at a neutral acceptor.[16–18] This possibility is excluded by our observation of the narrow no-phonon line in n-type material, where no neutral acceptors are present in equilibrium.

For lines above the $n=1$ exciton level, such as those from E_G, the $n=2$ exciton, and the Zn^0-exciton excited state, the intensities are affected by the fact that in photoluminescence excitons are formed by the binding of free charge carriers. The initial energy of these free carriers exceeds that of the final bound state so that intervening excited states may be traversed in the course of dissipation of the excess energy. The populations of excited states may, therefore, differ from thermal-equilibrium values.

Unidentified lines are present in the spectra. These lines are relatively weak and of unknown origin. The three lines between Zn^0-exciton triplet at 1.512 eV and its satellite at 1.506 eV (Fig. 4) are approximately equally spaced by 1.4-meV intervals below the 1.512-eV line. These might constitute resonant phonon replications of the 1.512-eV line; the resonance would have a lower frequency than for the Zn^--exciton complex as a consequence of the presence of an additional hole which would reduce the force constant. The line at 1.5172 eV seen in n-type material [Fig. 1(a)], and possibly in p-type [Fig. 1(c)], has remained too weak to allow much examination.

CONCLUSIONS

The free-carrier and $n=2$ free-exciton recombination lines have been observed in GaAs for the first time. This has been achieved by using epitaxial GaAs with an ionizable impurity concentration $<10^{15}$ cm^{-3}, by using a low intensity of illumination, and by reducing the sample temperature to 1.4°K. The band gap is $E_G = 1.5202$ eV$\pm$0.3 meV, and the $n=1$ exciton binding energy is $G(1)=4.7\pm0.4$ meV. The $n=2$ exciton line yields $G(2)=3.6\pm0.6$ meV. These observations agree with the data of Sturge[3] and of Wright and Galeener.[5] The low value of N_I in our epitaxial samples probably accounts for the reduction of Γ_i ($n=1$) to 1 meV from the value 7 meV found by Sturge for less pure, bulk samples.

Lines have been identified with acceptor-exciton and donor-exciton complexes. The theoretical work of Kohn,[12] Hopfield,[15] Sharma and Rodriguez,[2,14] and Munschy[13] has been valuable in predicting the binding energies of these complexes in terms of the ratio m_h^*/m_e^* and the impurity ionization energies. Our free-exciton and impurity-exciton binding energies are satisfied by $m_h^*/m_e^*\approx5$. The observed binding energies of the Zn^0 and Zn^--exciton complexes yield an acceptor ionization energy $E_A\approx26$ meV which agrees with experiment.[34] The identification of the Zn^0-exciton line has been confirmed by the observation of its exchange-split fine structure. Similar results were obtained for the Se^+-exciton complex ($E_D\approx6$ meV). The phonon wing of the Zn^--exciton line has been exhibited clearly. Again the best delineation is obtained at the lowest intensity of illumination. The dependence of this phonon wing on the illuminating intensity indicates that a resonant vibration of Zn in GaAs is involved.

These results show that the free-exciton and impurity-exciton spectra in GaAs are similar to those of wider band-gap semiconductors. For GaAs, however, much smaller binding energies are involved because of the small electron effective mass and the relatively large dielectric constants. Hence greater demands are placed on the perfection and purity of the specimens, and on the experimental technique.

ACKNOWLEDGMENTS

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[41] C. H. Henry, P. J. Dean, D. G. Thomas, and J. J. Hopfield, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), pp. 267–275; C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).
[42] R. C. C. Leite and A. E. DiGiovanni, Phys. Rev. **153**, 841 (1967).