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Radiative Lifetimes of Donor-Acceptor Pairs in *p*-Type Gallium Arsenide

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The behavior of the low-temperature emission spectrum of *p*-type gallium arsenide with changes in temperature and excitation intensity has been observed. The band, usually at ~1.49 eV (1.475 eV in germanium-doped samples), moves to higher energy as the pumping intensity or the temperature is increased. This behavior is consistent with a donor-acceptor-pair mechanism for the band. Radiative lifetimes and time-resolved spectra confirm this opinion. In high-purity crystals, the band decays in a fast but nonexponential manner, and the time-resolved spectra move steadily to lower energies as the delay after the pulse is increased. We believe these to be the first such measurements in gallium arsenide, and they firmly establish the origin of the 1.49-eV band. The properties of the decay are compared with those seen in GaP and CdS. The decay rate constant $W(0)$ in GaAs is estimated to be about 10^3 times greater than in GaP, and about the same as in CdS. The emission bands in the 1.50–1.51-eV region depend strongly upon the mode of excitation. The decay rates are high ($\tau<15$ nsec). Such short decay times are consistent with the annihilation of excitons or free-electron–bound-hole recombinations.

I. INTRODUCTION

The only absolute proof of the presence of donor-acceptor (D-A) recombination in semiconductors is the observation and cataloging[1–3] of the individual pair lines in the emission spectrum. When sharp lines are not seen, several less direct techniques are usually employed to identify band spectra with D-A transitions. These techniques depend upon (1) changes in band shape and in band peak energies as a function of excitation intensity, (2) changes in band shape and in band peak energies as a function of temperature, (3) radiative lifetimes of the D-A bands, (4) time-resolved spectra, taken after flash excitation of the sample, and (5) the growth of a new "high-energy band" which eventually dominates when the temperature is high enough, and which corresponds to a free-to-bound transition. Of these techniques, (1) and (2) have already been applied to emission bands in *n*-type GaAs. A typical spectrum[4] shows narrow emission bands near 1.51 and 1.49 eV. It is this latter band that has been the subject of these studies. Leite and DiGiovanni,[5] working with high-purity, *n*-type GaAs, have concluded after method (2) that the 1.49-eV band arises from the recombination of an electron trapped on a shallow donor with a hole on an acceptor. Yee and Condas,[6] using method (1), also attribute a 1.49-eV band to D-A recombination. In addition, there are other descriptions, based upon less certain grounds, that support[7,8] or oppose[9–11] this point of view.

In this paper we report the results of studies based upon all the techniques mentioned above. The samples were all *p*-type, and the free-carrier concentration ranged from 1×10^{15} to 2×10^{19}/cc. The deliberately doped samples contained zinc, germanium, cadmium, or silicon. Except for the last-mentioned dopant, for which no decision has been made, the conclusion reached is that the ~1.49-eV band (~1.475 eV in germanium-doped samples) is due to distant D-A recombination. The behavior of the bands in the vicinity of 1.51–1.50 eV is consistent with free- or bound-exciton decay and/or free-electron–bound-hole recombination. Anticipating the results of Secs. III and IV, we find that the emission in the 1.51-eV region depends upon the method of pumping. Under some circumstances one could be observing bound-exciton (or free-exciton) decay, while in other cases significant free-to-bound contributions are possible. This situation is consistent with the proposal of Cusano.[8] He separates the electron-beam-excited emission into three types: (a) 1.515 eV: band-to-band (one may add free excitons and bound excitons on shallow donors); (b) 1.505 eV: free-to-bound recombination; and (c) 1.49 eV: D-A recombination.

II. EXPERIMENTAL

The samples have been obtained from a variety of sources. Some are commercially available (zinc- or cadmium-doped, down to ~10^{16}/cc), whereas others (high-purity and germanium- or silicon-doped) were grown in these laboratories. Table I summarizes what is known about the samples discussed in this paper.

Spectra were obtained from samples at temperatures in the range 1.6–77°K. Liquid He, liquid H_2, and liquid N_2 were used as refrigerants. In-between temperatures were attained by use of an exchange-gas flow system. In this latter system, the temperature was recorded

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[1] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

[2] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, 269 (1964).

[3] F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, 1030 (1965).

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

[5] R. C. C. Leite and A. E. Di Giovanni, Phys. Rev. **153**, 841 (1967).

[6] J. H. Yee and G. A. Condas, J. Appl. Phys. **39**, 351 (1968).

[7] J. I. Pankove, J. Phys. Soc. Japan Suppl. **21**, 298 (1966).

[8] D. A. Cusano, Appl. Phys. Letters **7**, 151 (1965).

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

[10] E. W. Williams and D. M. Blacknall, Trans. Met. Soc. AIME **239**, 387 (1967).

[11] C. Benoit à la Guillaume and C. Tric, J. Phys. Chem. Solids **25**, 837 (1964).

TABLE I. Properties of the samples discussed in this investigation.

Sample	Total No. of donors/cc N_D	Total No. of acceptors/cc N_A	n, majority carriers/cc	Mobility μ 300°K (cm^2/V sec)	Resistivity ρ (Ω cm)
390-78	5.0×10^{15}	1.06×10^{16}	6×10^{15}	...	...
9-3A			1×10^{16}	...	5
148-0			2.6×10^{15}	5700	0.42
148-0 (Zn)			2×10^{19}	...	...
148A			2.6×10^{15}	5700	0.42

with a carbon resistor thermometer. The sample temperature at the point where the emission originated was not accurately known. In order to keep heating effects to a minimum, we used the lowest pumping levels that were consistent with good signal-to-noise ratios.

The excitation source was either an He-Ne laser (100 mW) or a pulsed molecular nitrogen gas laser. The latter emits a 7-nsec pulse with a peak pulse output of ~150 kW at 3371 Å.

The emission was analyzed by a 1-m Czerny-Turner grating spectrometer (8 Å/mm) and detected with a cooled RCA 7102 photomultiplier tube. For the lifetimes and the time-resolved spectra (TRS), the output from the 7102 was fed into either a Hewlett-Packard 185B sampling oscilloscope or a Tektronix 555 oscilloscope. The output cable from the phototube was terminated in such a way that the total decay time of the pulse and electronics was <10 nsec. The decay of the emission could be read from, or photographed on, the display tube of the oscilloscope, or else it could be plotted on a chart recorder as the sampling oscilloscope swept in time. The time-resolved spectra were obtained in a similar manner. In this case, however, the sampling oscilloscope was set at a particular time after the pulse (sampling interval 0.05 nsec) and the wavelength of the analyzing monochromator was scanned.

III. THEORETICAL FRAMEWORK

The radiative recombination of electrons bound to donors with holes trapped at acceptors has been shown to be an important mechanism of light emission in semiconductors.[1–3] For such D-A pairs at large separation, the energy of emission $E(r)$ is given approximately by

$$E(r)=E_g-(E_A+E_D)+e^2/\epsilon r\,, \qquad (1)$$

where E_g is the band-gap energy, E_A and E_D are the acceptor and donor binding energies, respectively, ϵ is the static dielectric constant, and r is the D-A separation. When r is small, individual line spectra may be seen. When r increases, the separation of these lines decreases and the emission usually merges into a broad band. Such spectra have been seen in several different semiconductors and they directly prove the presence of D-A recombinations.

TRS and perhaps radiative decay times provide the next best criteria by which to judge D-A pair spectra. In the limit of an isolated pair, the calculation of the radiative recombination rate $W(r)$ of an electron bound to a donor and a hole bound to an acceptor requires the evaluation of the optical matrix element between the state of the crystal with the electron and hole present and the state with them absent, i.e.,

$$W(r)\propto|M|^2\,, \qquad (2)$$

where

$$M=\int\Psi_f P\Psi_i\,d\tau\,.$$

Thomas, Hopfield, and Augustyniak[12] (THA) have further approximated this situation to the case where one particle is much more tightly bound than the other.[13] The wave function associated with the more tightly bound center is much more compact than that of the shallow center. In such a situation, and when band-to-band transitions are allowed (in GaAs and CdS but not in GaP), the expression for M reduces to a constant times an overlap integral S, where S is of the form

$$S=\int\Psi_e\Psi_h\,d\tau\,. \qquad (3)$$

The reaction rate $W(r)$ is then expressed as

$$W(r)=\text{const}\times(S)^2\,. \qquad (4)$$

When the electron is less tightly bound, this becomes

$$W(r)=W(0)e^{-2r/a}\,, \qquad (5)$$

where $W(0)$ is a constant and a is the Bohr radius of the donor.

With this model THA have demonstrated the form of the decay curves as a function of time, as a function of excitation intensity, and as a function of donor and acceptor concentrations. They found good agreement between this model and the C-S pair spectra in GaP. The values of $W(0)$ and a (of the acceptor) for C-S pairs in GaP, and for CdS[14] with unknown donors and

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[12] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, 202 (1965).

[13] They used C-S pairs in GaP, $E_C\sim40$ meV, $E_S\simeq107$ meV. In the original THA paper, the carbon acceptor was not correctly identified. At that time it was thought to be silicon.

[14] K. Colbow, Phys. Rev. **141**, 742 (1966).

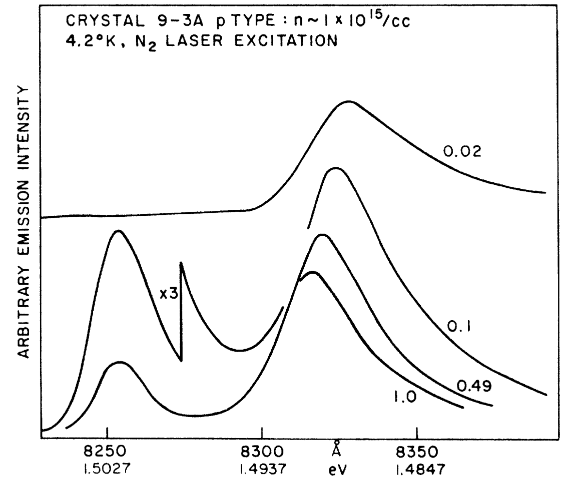

FIG. 1. Effect of excitation density upon the band positions and relative intensities in crystal 9-3A at 4.2°K. The fractional pumping densities are shown on each curve. The zero intensity levels have been shifted to make the figure easier to follow.

acceptors, are shown below:

GaP: $W(0)\simeq 5\times 10^5\ \text{sec}^{-1}$, $a=24$ Å (acceptor);

CdS: $W(0)\simeq 4\times 10^8\ \text{sec}^{-1}$, $a\simeq 30$ Å (donor).

If it is assumed that there is a random distribution of donors and acceptors, and if $N_D>N_A$ and no redistribution of holes or electrons takes place, then the total D-A emission is given by the decay of the neutral acceptors and has the form

$$I(t)=I(0)f(W(0),N_D,E_D,t). \qquad (6)$$

In the case of p-type GaAs, where $N_A>N_D$ and $E_D<E_A$, this becomes

$$I(t)=I(0)f(W(0),N_A,E_D,t). \qquad (7)$$

Since GaAs has a direct band gap, $W(0)$ is likely to be large, and we expect a rapid decay. THA have shown quantitatively how the concentration of the majority carrier will influence the decay rate. If $N_D>N_A$ or if $N_A>N_D$, then the higher the concentration, the shorter the lifetime. When $N_D\sim N_A$ the situation is more complex, but at high doping levels compensation has the effect of reducing the decay rate considerably. At low concentrations—$N_A,N_D\sim 10^{15}$/cc—the decay rate is influenced very little by compensation. With the majority of samples used here it would appear (Table I) that we are in this latter regime.

The donors in GaAs are very shallow, $E_D<10$ meV. With a hydrogenic model, the Bohr radius can be 100 Å or more. Thus from Eq. (5) we expect $W(r)$, $r=200$–400 Å, to be orders of magnitude greater than in CdS, where $E_D\sim 30$ meV. Furthermore, with such shallow donors, at some concentration[15] an impurity band will normally form. At that doping level the mobility of the "trapped" electron will increase greatly, and in the limit this D-A recombination will become a type of free-to-bound transition. Thus, at early times, the close D-A pairs will recombine as normal pairs, although after a certain time it will be easier for the electron to move through the crystal until it gets to some critical distance r_c from a neutral acceptor, at which point the hole and electron will recombine. The value of r_c will depend upon several interacting conditions, but the net result will be the disappearance of many of the pairlike characteristics in the emission. The lifetimes, for instance, will become a function of the rate of hopping, which is very temperature-dependent, rather than of the initial D-A separation.

Even in high-purity p-type crystals where banding due to donors has been reduced, there will still exist this hopping mechanism, whereby unreacted carriers can seek out a favorable site from which to recombine. Even so, the interdonor overlap should be small (an average r_{D-A} of >300 Å results if there are about 5×10^{15} impurities/cc), and fairly normal D-A recombination may obtain. There seems little doubt, however, that the rate of recombination will be high.

IV. EXPERIMENTAL RESULTS

We describe in detail the results for four crystals: 9-3A, 148A, 148-0, and 390-78. When the crystals are pumped hard at low temperatures the emission spectrum generally consists of two main peaks. In the first three crystals, which were not intentionally doped,

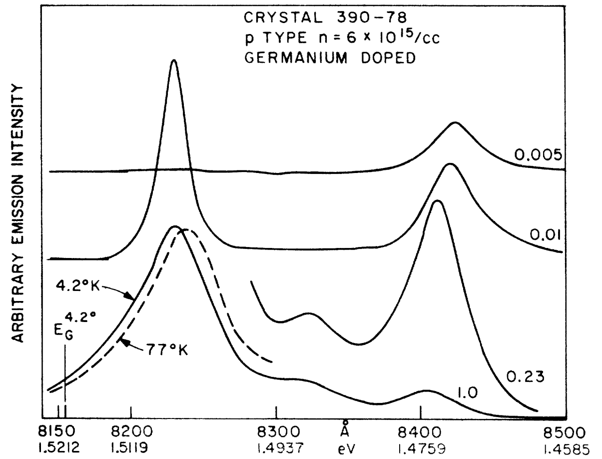

FIG. 2. Effect of excitation density upon the band positions and relative intensities in crystal 390-78 at 4.2°K.

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[15] In CdS, ESR experiments on donors show that this situation is established at $n\sim 10^{17}$/cc. Hence, in GaAs it is likely to be reached with $n<10^{17}$/cc.

the peaks are at 1.50–1.51 eV[16] (8200–8250 Å) and 1.49 eV (~8330 Å), with the latter repeated at lower energies via weak LO-phonon coupling. The germanium-doped sample 390-78 has, in addition, a band at 1.475 eV (~8400 Å) which we believe to be characteristic of the germanium acceptor.

A. Influence of Excitation Intensity on Emission

Figures 1 and 2 show spectra taken with various excitation intensities. It is evident that the 1.49- and 1.475-eV bands move to lower energies as the excitation intensity is attenuated. The 1.51-eV bands change shape as the excitation is reduced, but the peak does not shift (except for a small movement to higher energy that is seen in some cases). This latter shift could be due to heating of the crystal at high pumping levels. Since this shift is in the opposite sense to that seen for the 1.49- (1.475-) eV band, we conclude that the 1.49- (1.475-) eV band shift is a genuine result of varying the excitation intensity at constant temperature. Both methods of excitation (N_2 laser or He-Ne laser) give similar shifts, the rate of movement being ~1 meV per tenfold change in excitation intensity. At the highest pumping levels (N_2 laser) the shift rate is higher than at lower pumping levels.

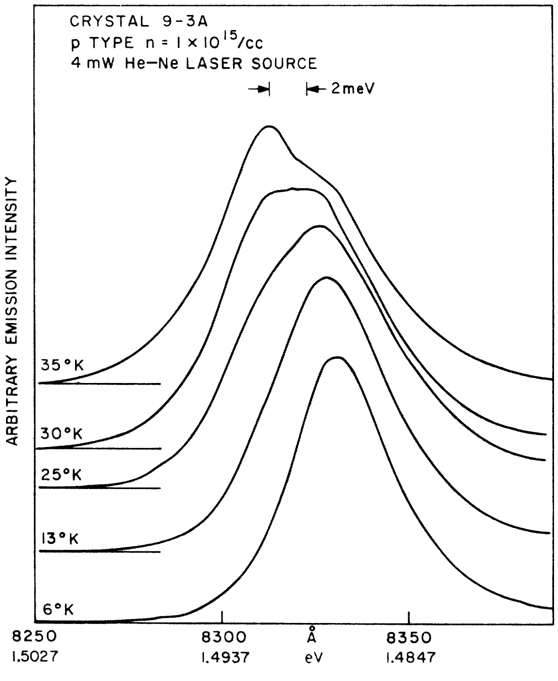

FIG. 3. Variation of the 1.49-eV (~8330-Å) band parameters with temperature (crystal 9-3A). Note the appearance of a second band on the high-energy side at higher temperatures. In this temperature range E_g is nearly constant.

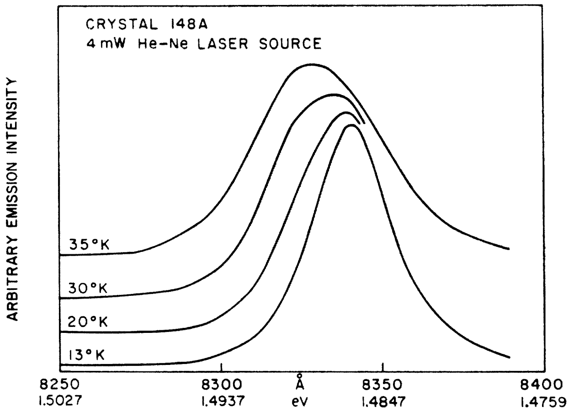

FIG. 4. Temperature effect upon the shape of the 1.49-eV band in crystal 148A. In this case, there is no distinct high-energy band; contrast Fig. 3.

It is well established that close pairs decay more rapidly than distant pairs. Increasing the excitation intensity will favor the closer pairs, and according to Eq. (1) the band peak will move to higher energies. In GaP, where the distant D-A transitions are relatively easy to saturate, the pair bands move ~3.5 meV per tenfold excitation-intensity change. In the present case, the slower rate of shift has two causes. First, the transition rate is much higher than in GaP, and saturation is much harder to achieve. Secondly, in high-purity crystals, because the average D-A separation is large, $e^2/\epsilon r$ varies much less than in crystals with high impurity content. The crystals used here have one or two orders of magnitude fewer impurities than do typical GaP crystals used by THA.

The variation of the emission intensity with excitation changes confirms these opinions. The 1.49- (1.475-) eV band intensity is almost a linear function of excitation density, again indicating that efficient saturation of distant pairs could not be achieved. This, it should be noted, takes place in high-purity crystals where the low impurity concentration should favor saturation.

B. Influence of Temperature upon the Spectrum

Figures 3–5 show measurements up to about 40°K. In this region, the band-gap energy E_g is only a slowly varying function of temperature. E_g decreases with increasing temperature (see Fig. 5 for the 77°K band position). The movement of the lower-energy bands (1.49 or 1.475 eV) to higher energy with increasing temperature must arise from a genuine increase in the average transition energy of the band with increasing temperature.

One further aspect, seen clearly in Fig. 3, is the appearance of a new band on the high-energy side of 1.49 eV as the temperature is raised. Quantitative intensity-versus-temperature measurements are difficult to make because of inaccuracies in the temperature

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[16] The position of this band depends upon whether the excitation source is the N_2 laser or the He-Ne laser. For convenience, we will continue to refer to this emission as the 1.51-eV band. The detailed behavior of these bands at high excitation levels is to be treated in a subsequent paper.

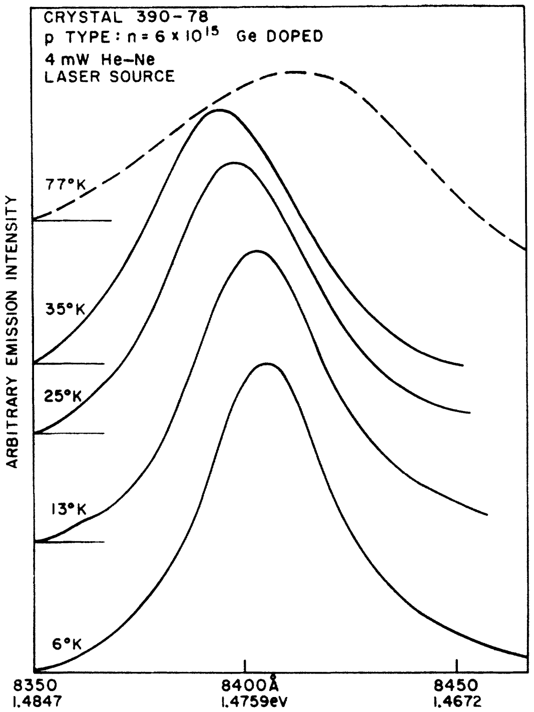

FIG. 5. Temperature effect upon the band shape and peak energy of the 1.475-eV (~8400-Å) band in the germanium-doped crystal 390-78. The 77°K band position illustrates the effect of the band-gap variation at higher temperatures.

estimates (Sec. II), and also because the bands overlap strongly and resolution is difficult. The peak of the new band is 3.0±0.5 meV above the original peak and appears to be the band recently discussed by Shah, Leite, and Gordon.[17] We are not able to provide a detailed comment upon its origin because we lack sufficiently precise data. It presumably arises from free-to-bound or excited-state–donor—ground-state–acceptor pair recombination. In either case its very appearance is strong evidence in support of the D-A model for the 1.49-eV band.

The movement of the 1.49- (1.475-) eV band with temperature is again that expected for D-A pair recombination. Hence, at higher temperatures, unreacted carriers can be released thermally from their donor sites, and they then migrate to a more favorable site from which to recombine. At intermediate temperatures a thermally increased hopping mobility will have the same effect. Again, this effectively reduces the value of r in Eq. (1), leading to a higher energy for the band peak. As has been noted in other works,[5] the 1.51-eV band increases in intensity as the temperature is raised, whereas the 1.49-eV band intensity decreases. The increase can be understood if trapped carriers that are responsible for the 1.49-eV band are released to the conduction band at higher temperature and then decay, in a variety of ways, to give the 1.51-eV band. The process that leads to the 1.51-eV bands is favored by high excitation intensities and high temperatures, whereas the opposite is true of the deeper 1.49- (1.475-) eV bands. The intensity of the 1.49-eV band falls rapidly in the range 30–40°K. This is consistent with the release of carriers from the more shallow impurity, and a binding energy of about 3–4 meV can thus be estimated. This result is consistent with that reported by Leite and DiGiovanni.[5]

C. Radiative Lifetimes Using N_2 Laser

Lifetimes have been measured in a number of *p*-type crystals, and the rate of recombination at all emission energies is high. In the more heavily doped crystals the emission decays with a lifetime $\tau < 15$ nsec. In such cases no further information could be obtained, since this lifetime rivals the fall time of the apparatus. In *all* crystals examined, the 1.51-eV band decayed in this manner (Figs. 6–8 show examples).

As the nominal impurity level decreases, the decay rate of the 1.49-eV band becomes noticeably slower. Figure 8 gives a quantitative example of this concentration effect. The lightly doped sample 148-0 shows a moderately slow decay of the 1.49-eV band, whereas in

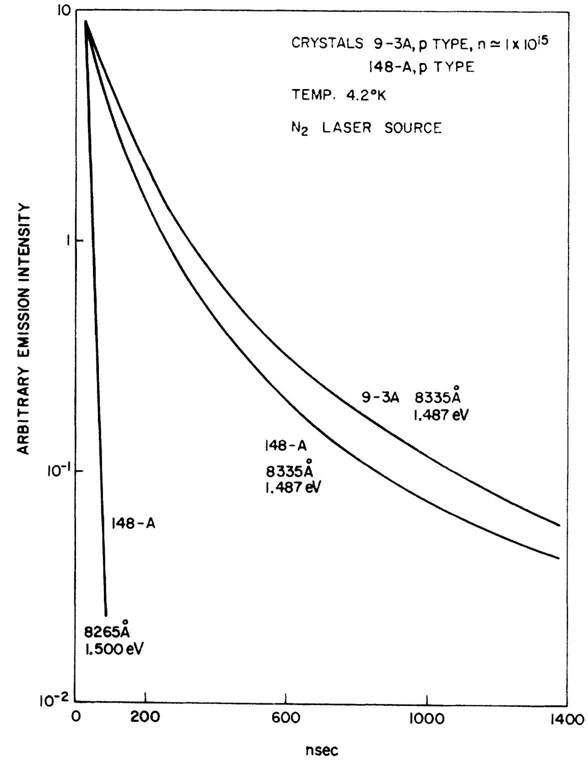

FIG. 6. Individual band decays for crystals 9-3A and 148A at 4.2°K. The decay in the region of 1.50 eV is essentially an upper limit for the time constant of the apparatus. The nonexponential nature of the 1.49-eV band decay is evident.

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[17] J. Shah, R. C. C. Leite, and J. P. Gordon, Phys. Rev. **176**, 938 (1968).

the deliberately doped sample 148-0 (Zn), the decay rate is much faster. The peak of the 1.49-eV emission band moves to higher energy in the more heavily doped crystal [see Eq. (1)]. In less-well-controlled, heavily doped samples the 1.49-eV band decays as rapidly as the 1.51-eV band shown in Fig. 8. The transition might be better represented as a free-to-bound transition (Sec. III) at such high impurity concentrations. The measurements shown in Figs. 6–8 were made by sampling a 5-Å slot in the spectrum near the peak of the emission band. Since the band is 25–30 Å in half-width, this result does not represent the whole of the band decay. At the same time, since the band maxima do not exhibit large energy shifts in the time-resolved spectra (see Sec. IV D), the above results are fairly good approximations to the total band decay. That this is so is shown by Figs. 9 and 10, which illustrate the decays of the total emission (taken in zero order with filters that could not discriminate against 1.51 eV). If the decay of the 1.51-eV band is as rapid as we believe ($\tau \lesssim 10$ nsec) and is exponential, then its intensity is down by $>10^5$ after 100 nsec, and the decay thereafter is again due to the much slower 1.49- (1.475-) eV band. The scale in Fig. 9 is such that at >200 μsec the intensity seems to have a nearly exponential decay. In actual fact, at large t the band decays as $t^{-1.3}$, to a good approximation. The intensity shown in Fig. 10 is diminishing as $t^{-1.8}$ at large t. As shall be seen in Sec. V, these decay rates at large t can be correlated with the purity and relative donor-acceptor concentration in each crystal.

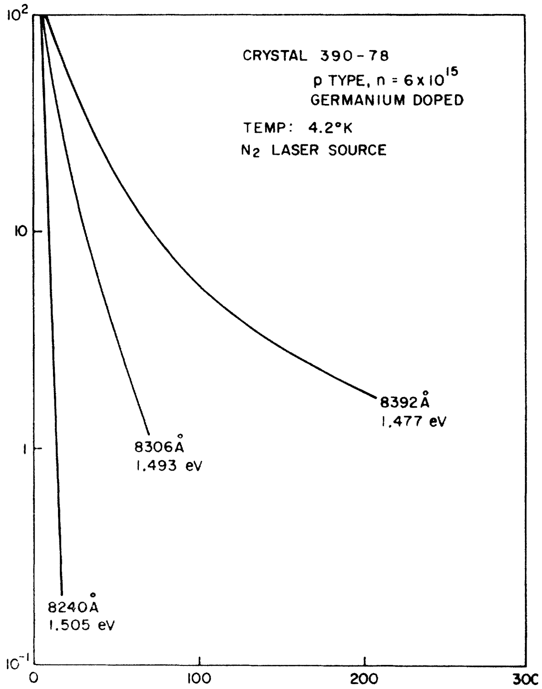

FIG. 7. Individual band decays for crystal 390-78 at 4.2°K. The origin of the band at 8306 Å is not known. The nonexponential nature of the 1.475-eV band is again evident.

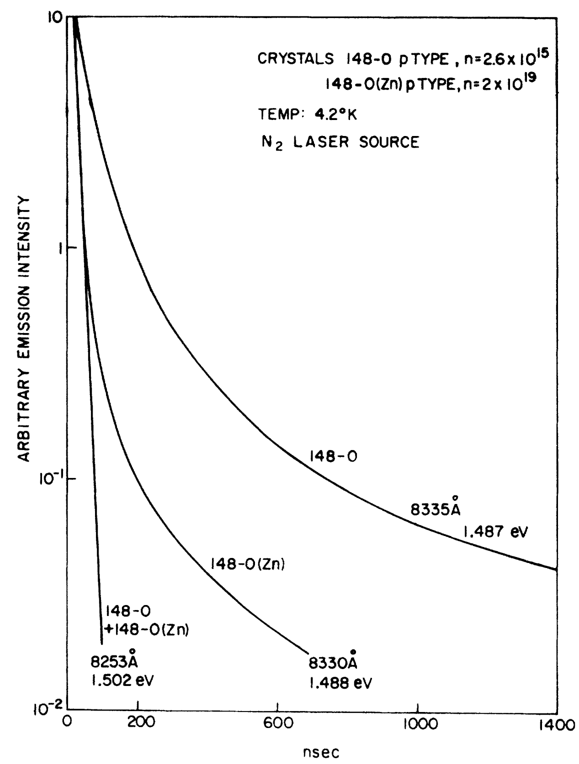

FIG. 8. Individual band decays for crystal 148-0 both with and without added zinc impurity. The dramatic effect of impurity concentration upon the decay rate of the 1.49-eV band is shown. The band peak shifts slightly to higher energies in the more heavily doped sample as predicted by Eq. (1) in the text.

In summary, it is clear that radiative lifetimes in GaAs are typically in the nanosecond to microsecond range. The bands near 1.51 eV are always fast and have lifetimes $\tau \leq 15$ nsec. In high-purity samples the lifetimes of the 1.49- (1.475-) eV bands can be much longer. In all cases examined the 1.49-eV band decay exhibited nonexponential behavior. The concentration dependence of the lifetimes of these bands has been established and it is in accordance with existing theories.[12]

D. Time-Resolved Spectra Using N_2 Laser

The measurement of time-resolved spectra (TRS) in our particular arrangement is tedious. The results are recorded on a point-by-point basis and they have not been obtained for all crystals. Figure 11 shows a typical set of results. The 1.49-eV band moves steadily to longer wavelengths as the time delay after the pulse is lengthened. Except at very short times,[18] the emission band always has $\Delta\nu_{1/2}\sim 5$ meV, as compared with $\Delta\nu_{1/2}\sim 5.5$–

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[18] Although the broadening seen on the high-energy side of the band could be due to close D-A pair recombination, the proximity of the tail of the 1.51-eV bands makes it difficult to assert this point. In all likelihood, some of the broadening is D-A in origin.

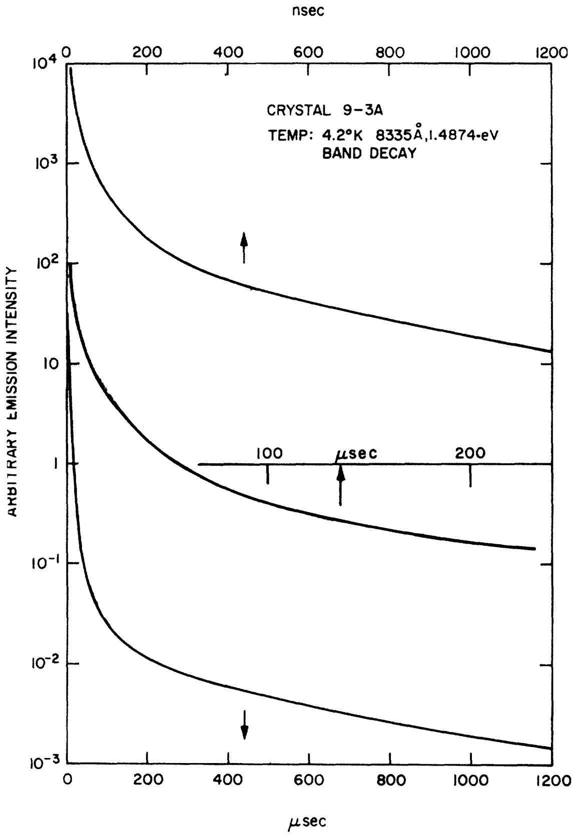

FIG. 9. Intensity-versus-time plot for the decay of the 1.49-eV (8335 Å) band in crystal 9-3A at 4.2°K. At very short times (<100 nsec) the intensity is mostly from the 1.51-eV band, but beyond 100 nsec it is from the 1.49-eV band only. At large t the decay follows the law $I \propto t^{-1.8}$ (see text).

6.0 meV in regular photoluminescence measurements. The band peak moves some 4.5 meV in 3.4 μsec. Assuming $E_D = 6.5$ meV and $E_A = 28.5$ meV (see below), the $t \approx 0$ sec band maximum corresponds to pairs about 150 Å apart, whereas at $t = 5$ μsec, the spectrum represents pairs separated by an average distance of about 450 Å. The lower limit on the D-A separation is consistent with the large donor Bohr radius (≈ 100 Å). After only 1600 nsec the peak of the TRS is already below the normal photoluminescence emission peak position and the rate of shift of the peak is quite slow.

These observations are consistent with the properties of the crystals used here. The absence of very narrow TRS at large t is attributed to the highly compensated nature of the crystals (see Sec. V). The relatively small shift of the band peak in the TRS arises from two causes. First, really close pairs ($r < 100$ Å) do not exist in GaAs, and it is the *presence* of these pairs that gives rise to the large shifts seen in the GaP TRS. Secondly, the compensation of the GaAs crystals is expected to broaden towards high energy the TRS obtained at large t. This will tend to reduce the magnitude of the observed shift. Finally, with a very shallow impurity in a direct-gap material, saturation will be difficult because of the high decay rate. With these qualifications, the results are again these expected of D-A recombination.

V. DISCUSSION: 1.49- AND 1.475-eV BANDS

The results found for these bands confirm the earlier proposals[5,6] (for n-type material) that this emission arises from D-A recombination. Thus, increasing the excitation intensity tends to saturate the more distant pairs, and a greater proportion of the emission comes from closer pairs. By Eq. (1) this moves the band maximum to higher energy. Flash excitation usually brings about a considerably smaller shift than continuous pumping because the close pairs are populated only once in each flash. In the present case, flash excitation from the N_2 laser ($>10^{15}$ photons/pulse) gives rise to a shift that is quite similar to that found with the He-Ne laser. The reason for this similarity is believed to be that the levels of excitation that can be reached, even with continuous pumping, are not high enough to efficiently saturate the rather rapidly decaying distant pairs. The small shifts per unit pumping-intensity change substantiate this point of view. Moreover, in the spectra recorded here, we did not see the type of pair-band *shape* encountered in GaP[12] at high pumping levels. This is not surprising, because in high-purity GaAs crystals where few really close pairs exist, the spectra that are obtained are equivalent to those seen in GaP TRS at large t (i.e., when r is large). In CdS, where the rate of decay is more like that found in GaAs, spectra with similar characteristics are observed.[14] Part of the broadening seen at short times or at high excitation intensity in GaP has another origin: the overlap of the phonon-assisted decay of very close pairs with the no-phonon emission of more distant

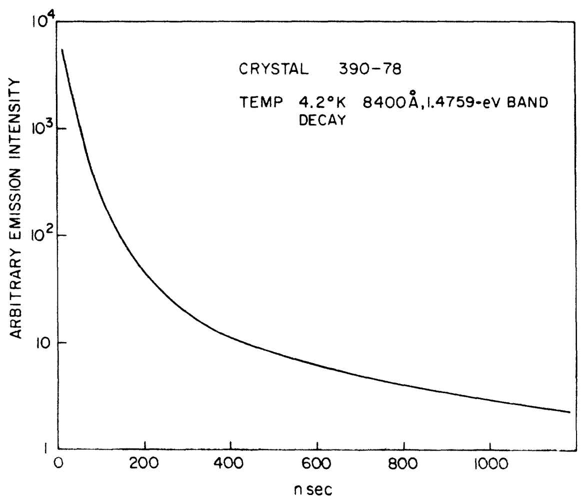

FIG. 10. Intensity-versus-time plot for the decay of the 1.475-eV (8400 Å) band in crystal 390-78 at 4.2°K. At large t the decay goes as $I \propto t^{-1.8}$.

pairs. In GaAs this is not a problem because phonon coupling is weak, and, in addition, the no-phonon lines of close pairs would fall above the band gap if the LO-phonon-coupled emission were to fall in the region of 1.49 eV.

Raising the temperature leads to energy shifts similar to those found when the excitation intensity is increased. Leite and co-workers[5,17] have given good discussions of these temperature-dependent spectra, both for the case where the band simply broadens towards high energy[5] and for the case where a new temperature-sensitive band appears.[17] We have shown examples of both types of behavior (Figs. 3 and 5). The most important point here is the appearance of the high-energy band as the temperature is raised. Whether that band arises from free-to-bound transitions or from recombination between excited donors and ground-state acceptors, its very presence is strong evidence[14] for the D-A origin of the low-temperature 1.49-eV band.

The TRS and lifetimes provide the most compelling reasons for accepting a D-A origin for the 1.49- and 1.475-eV bands. The results are in good qualitative accord with the THA theory. No attempt at a quantitative fit has been made.

Because of the small majority-carrier concentration, the lightly doped crystals are probably compensated to the point where the THA $N_D \approx N_A$ model will apply. At long times after the flash, the decay is expected to go as t^{-2} in heavily doped compensated crystals and as t^{-1} in lightly doped ($<1\times10^{15}$/cc) samples (compensated or not). In crystal 9-3A the decay can be followed over seven decades in intensity, and at large t it is decaying as $t^{-1.3}$. Hence this crystal appears to be in the lightly doped region (Table I). Crystal 390-78 decays more rapidly than 9-3A, and at the extreme is going as $t^{-1.8}$. Thus the Hartree hopping limit[12] seems to be appropriate, and the decay rate is dominated by the rate of hopping rather than by the optical decay rate. The difference in the decays of these two crystals is rather puzzling, since from Table I one would expect them to be similar. At large t other complications can develop,[12] and the exact significance of these decay rates may be in doubt.

The TRS are not very narrow and they do not move over large distances in the time interval available to us. This has been discussed in earlier sections, and is readily attributed to the compensated state of the crystals, to the large Bohr radius of the donor, to the allowed nature of the D-A spectra, and to the high purity of the crystals.

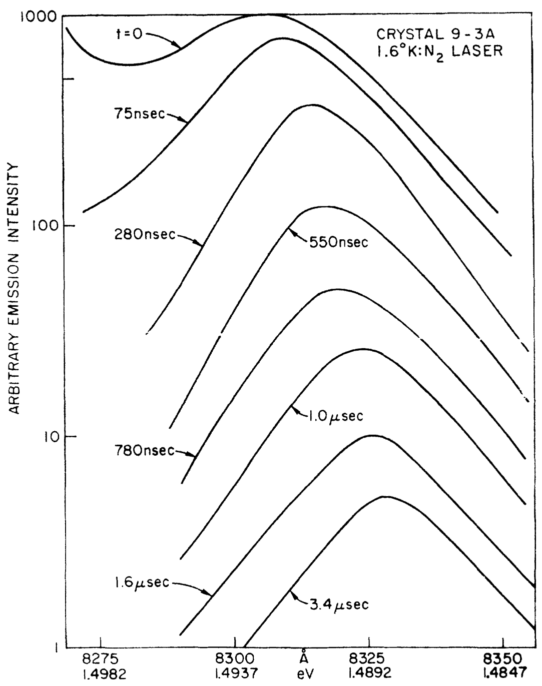

FIG. 11. Time-resolved spectra taken from crystal 9-3A at 1.6°K. The shift of the band peak with time is clearly shown, as is the broadening of the high-energy side of the band at small t (see text).

Associating approximate binding energies $E_D = 6.5$ meV and $E_A = 28.5$ meV with the D-A pairs in 9-3A, one can evaluate an approximate $W(0)$.[19] This process is somewhat arbitrary because donor and acceptor binding energies are not available with any certainty. At any rate, using the above values, one derives a fairly constant value of $W(0)$. This is $W(0) = (3\pm2)\times10^8$ sec^{-1}. Compared with the value of $W(0)$ calculated[14] for CdS, the presently obtained value is very reasonable. The rate of decay $W(r)$ depends upon E_D as well as $W(0)$. When E_D in CdS and GaAs are included, the rate $W(r)$ at $r \approx 300$ Å is about 10^6 times faster in GaAs than in CdS, which in turn is about 10^4 times faster than GaP.

In recently available high-purity, epitaxially grown GaAs, sharp lines are found[20] in the 1.50-eV region. A successful analysis of these spectra, and correlations with known impurities, may be anticipated. This will then lead to a better understanding both of these spectra and of the nature of the D-A pairs responsible for the spectra discussed here. Gilleo *et al.*[20] have already associated a binding energy of 26 meV with the neutral zinc acceptor and they propose selenium as a shallow donor, $E_{Se} \simeq 6$ meV. These values are close to those needed to give a consistent $W(0)$ in 9-3A; therefore

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[19] Although $W(r)$ is very sensitive to E_D [Eq. (5)], it turns out that $W(0)$ is much more dependent upon E_A than on E_D. This is because in the equation used to derive $W(0)$, $\ln[W(0)t] = 4E_D/E_c + \ln(1-E_c/E_D)$, where $E_c = e^2/\epsilon r$, E_D and E_c enter as ratios whereas E_A enters only in the initial evaluation of E_c. At constant E_A, increasing (decreasing) E_D increases (decreases) E_c, and the resultant $W(0)$ is a slowly varying function of E_D, remaining within $(3\pm2)\times10^8$ sec^{-1} when E_D is in the range 5–8 meV. The dependence of $W(0)$ on E_A (through E_c) is much sharper, and the best value of E_A is 28.5 ± 0.5 meV. Obviously, values of E_D obtained in this manner are subject to considerable error.

[20] M. A. Gilleo, P. T. Bailey, and D. E. Hill, Phys. Rev. **174**, 898 (1968).

these impurities may well be involved in the 1.49-eV D-A spectra. Further support for this contention can be gained from the following: Gilleo *et al.*[20] have also observed emission in the region of 1.49 eV. In zinc- and selenium-doped samples, $p=1.5\times10^{14}$/cc, the emission is very sensitive to the intensity of excitation. At high pumping levels the ~1.49-eV emission has the form of a band about 10 meV wide with a sharp spike in the leading edge. At low pumping levels there are two well-resolved peaks, one at 1.489 eV ($\Delta v_{1/2}\sim1$ meV) and the other at 1.486 eV ($\Delta v_{1/2}\sim3$ meV). It is evident from their results that this latter peak is very sensitive to the level of excitation, a shift of about +1 meV per tenfold increase in excitation being observed. Regardless of the interpretation of the sharp 1.489-eV line, the position and width of the 1.486-eV band and its sensitivity to excitation intensity support a model that attributes it to D-A recombination. Gilleo *et al.*[20] assign the band to a phonon wing associated with the 1.489-eV line.

Electrical measurements[21] have identified germanium as a deep acceptor in gallium arsenide. Recent work, based upon optical and electrical measurements,[22,23] provides a value of $E_A\sim36$ meV. This latter value is consistent with what is found in 390-78, and the donor associated with the 1.475-eV band must be very shallow.

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Diffusion and Solubility of Cu in CdS Single Crystals*†

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Measurements have been carried out on the rate of diffusion of Cu in CdS single crystals. The temperatures covered ranged from 146 to 400°C, well below those covered by previous diffusion investigations. The method of measurement employed the compensation of high-conductivity n-CdS by the in-diffusion of Cu acceptors. The thickness of the compensated layer was calculated from capacitance measurements. Diffusion coefficients have been calculated explicitly for diffusion parallel to the c axis from the compensation depth and the complementary error function. These values ranged from $\sim10^{-14}$ to 10^{-10} cm^2/sec, with an activation energy of 0.96 ± 0.05 eV and $D_0=2.1\times10^{-3}$ cm^2/sec. The solubility of Cu in CdS was determined by both colorimetric and spectrographic analysis for Cu content in diffusion-saturated CdS granules. The result found was $[\mathrm{Cu}]=6.6\times10^{22}e^{-(0.505\ \mathrm{eV})/kT}$. A marked anisotropy was found which favored diffusion of the compensated layers perpendicular to the c axis by one to two orders of magnitude. Increasing the edge-dislocation density parallel to c by bending a crystal around the c axis significantly increased the diffusion rate in that direction. For this reason, the observed anisotropic behavior is ascribed to preferential orientation of dislocations perpendicular to the c axis. However, the total Cd vacancy content of the dislocations, $\sim10^{12}$ cm^{-3}, could not act as the source for regeneration of Cd vacancies required for compensation. It is therefore tentatively concluded that Cu diffusion along the dislocations, together with thermal regeneration of Cd vacancies coming from voids (precipitated sulfur vacancies) in the bulk, is the primary mechanism of Cu compensation of CdS crystals.

I. INTRODUCTION

COPPER is known to act as a deep acceptor in CdS; this property causes Cu compensation to be of considerable interest in CdS semiconductor devices. Furthermore, it is possible to study the diffusion of Cu in CdS by converting conducting n-type CdS to high-resistivity material. The diffusion coefficient of Cu in CdS has previously been measured by tracer[1,2] and optical-absorption[3] techniques in the 300–750°C range. However, it is known that Cu diffuses readily in CdS devices at much lower temperatures. It is not clear that these high-temperature results can be extended accurately over several orders of magnitude of the diffusion coefficient to the lower temperatures; such an extrapolation predicts, for example, that CdS solar cells should rapidly develop a prohibitive series resistance and should therefore degrade quickly at 150°C due to Cu diffusion. Some increases in resistance are indeed ob-

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