PHYSICAL REVIEW VOLUME 170, NUMBER 3 15 JUNE 1968

Temperature-Dependent Radiative Recombination Mechanisms in GaP(Zn,O) and GaP(Cd,O)†

J. D. Cuthbert
Bell Telephone Laboratories, Whippany, New Jersey

AND

C. H. Henry and P. J. Dean
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 2 February 1968)

Henry *et al.* have shown that the low-temperature red luminescence in both GaP(Zn,O) and GaP(Cd,O) is composed of a bound-exciton band overlapped at lower energies by a new type of long-lived pair band. This paper describes a study of the temperature dependence of the spectral positions and time-decay characteristics of these red bands. The samples were excited with electrons from a pulsed accelerator, and the bands were studied by time-resolved spectroscopy in the range 1.7–300°K. At low temperatures the intensity ratio of the pair and bound-exciton bands is dependent upon sample preparation and excitation intensity. Regardless of the initial value of the ratio, the exciton emission becomes dominant in a transitional temperature range between 60 and 120°K. At room temperature the emission is almost entirely excitonic. The accompanying large changes in the spectral and time-decay characteristics are semiquantitatively explained by a theory based on the assumption of thermal equilibrium of holes amongst the exciton-hole, acceptor, and valence-band states. Luminescence excitation measurements in GaP(Zn,O) were used to estimate the concentrations of Zn-O complexes which were correlated with relative luminescence efficiencies and melt compositions.

I. INTRODUCTION

RECENT studies[1–3] of the low-temperature red luminescence in gallium phosphide doped with Zn and O or Cd and O [GaP(Zn,O) and GaP(Cd,O), respectively] revealed that, in both cases, the emission is composed of two overlapping bands. Previous investigators were unaware of this major complication.[4–6] The recent experiments established that the red bands arise from the formation of nearest-neighbor Zn-O or Cd-O donor-acceptor pair complexes. The concentration of these nearest-neighbor substitutional complexes is much greater than anticipated for a random distribution of donors and acceptors and indicates that preferential pairing occurs on the nearest-neighbor sites.[7] The Cd-O and Zn-O complexes act as deep electron traps. After trapping an electron at low temperatures, the complex becomes negatively charged and can trap a hole by Coulomb attraction. The electron and hole then decay as a bound exciton and produce the "bound-exciton band." If a hole is not trapped, the electron will eventually recombine with a hole on a distant acceptor. This recombination results in the "pair band" lying somewhat lower in energy than the bound-exciton band. The energy levels and transitions are indicated in Fig. 1.

In contrast with the bound-exciton luminescence, the pair luminescence persists for long times after pulse excitation and, in this respect, resembles the well-known "green" donor-acceptor pair recombination in GaP.[8] In the red pair bands, however, there is no electrostatic energy contribution $e^2/\epsilon r$ to the photon energy, so that the distinctive series of sharp lines normally present in donor-acceptor pair spectra is missing.

The pair band and the bound-exciton band are broadened primarily by the phonon coupling of the deeply

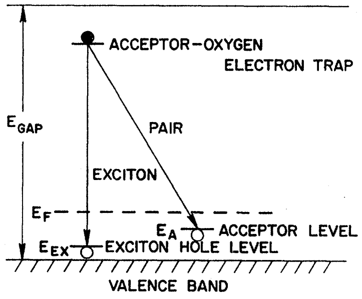

FIG. 1. Energy-level diagram showing the transitions that give rise to the bound exciton and pair luminescence bands in GaP(Cd,O) or GaP(Zn,O). Electrons are trapped at Cd-O or Zn-O complexes. Holes are trapped either at free Cd or Zn atoms (level E_A) or at negatively charged Cd-O or Zn-O complexes (exciton-hole level E_{ex}).

---

† Research sponsored in part by the Cambridge Research Laboratory, Office of Aerospace Research, under Contract No. AF19628-67-C-0147.

[1] C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).

[2] T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968).

[3] P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. **168**, 812 (1968).

[4] M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **36**, 1528 (1965); **37**, 483 (1966).

[5] D. F. Nelson and K. F. Rodgers, Phys. Rev. **140**, A1667 (1965).

[6] J. A. W. Van der Does de Bye, Phys. Rev. **147**, 589 (1966).

[7] From the intensity of the Zn-O infrared pair band see Ref. 3 and the saturation of this band it is estimated that the concentration of isolated oxygen is less than 5×10^{17} atoms/Cm^3. Therefore the concentration of 5×10^{16} Zn-O nearest-neighbor pairs, reported later in this paper, must be due to preferential pairing.

[8] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

trapped electron, so that both bands have approximately the same shape and half-width of about 135 meV. They are separated by the difference in the binding energies of a hole trapped on an exciton or on an acceptor. The small energy separations, 25 meV for GaP(Zn,O) and 60 meV for GaP(Cd,O), result in extensive overlap of the bands.

This paper describes a detailed study of the temperature dependence of the spectral position and time-decay characteristics of the red luminescence. At low temperatures, the intensity spectrum is quite sample-dependent. Whether the red luminescence is dominated by the pair band or bound-exciton band depends upon the number of neutral acceptors available for pair decay. In general, low acceptor concentrations favor the bound-exciton band and high concentrations, the pair band. Because the density of exciton-hole states is proportional to the excitation intensity, the intensity spectrum at any acceptor concentration depends on the excitation intensity. Therefore, intense excitation favors the bound-exciton band and weak excitation, the pair band. In heavily *p*-type GaP(Zn,O) it is believed that hole-tunneling effects cause the bound-exciton decay to dominate the luminescence even for weak excitation.

At high temperatures, up to 300°K, the time-decay characteristics and spectral position of the red luminescence show that the bound-exciton band dominates the emission of both GaP(Cd,O) and GaP(Zn,O) crystals regardless of acceptor concentration and excitation intensity. This is explained by the much larger transition probability for exciton over pair decay and by the assumption of a thermal equilibrium distribution of holes among the hole states at elevated temperatures.

Also discussed are absorption spectra of the bound-exciton transitions obtained by luminescence excitation and measurements of the red-luminescence efficiency. These measurements have provided information on the densities of Cd-O and Zn-O complexes and insight into the doping conditions for optimal luminescence efficiency.

II. EXPERIMENTAL TECHNIQUES

Time-resolved spectra and luminescence decay times in the liquid-hydrogen and helium ranges were recorded in the following manner[9]: The samples were repetitively excited in the refrigerants by 100-nsec electron pulses from a Van de Graaff accelerator operating at 300 keV. The maximum current density at the sample was about 0.1 A/cm^2. The luminescence pulses were dispersed by a Spex f/6.8 scanning spectrometer and detected at the output slit by an RCA 7102 photomultiplier. The S-1 photocathode and blaze of the grating provided a spectral response constant to within 10% over the red-wavelength range. The photomultiplier output was displayed on a Tetronix 564 sampling oscilloscope triggered coincidentally with the arrival of the electron pulses at the sample. For time-resolved spectra, the analog output of the oscilloscope, proportional to the luminescence intensity $I(t)$ at a time t defined by the setting of the sampling window, provided the Y deflection; the wavelength analog voltage from the spectrometer provided the X axis deflection of an X-Y recorder. Luminescence-decay curves for a given spectrometer wavelength setting were obtained by using the same arrangement but with the time analog voltage from the sampling oscilloscope applied to the X axis of the recorder.

Although the over-all luminescence efficiency of the samples was usually high, the large breadth of the red bands compared with the 7 Å resolution used for recording the spectra resulted in relatively weak photomultiplier signals. The necessity of using a photomultiplier detector with an S-1 photocathode having a quantum efficiency of less than 1% accentuated this problem. It was therefore found desirable to sometimes reduce the bandwidth of the system to provide more sensitivity by using a cathode follower and variable load resistors at the photomultiplier output. Care was exercised not to distort the pulse shape in the time interval of interest.

The study of samples at temperatures in the range between 20 and 300°K was facilitated by a specially constructed variable temperature Dewar. The samples were again excited by energetic electrons which passed into the Dewar through a stainless-steel window. The samples were maintained at a given temperature by forced convection of helium gas at the appropriate temperature. Pilot experiments showed that this scheme enabled the heat dissipated in the sample to be effectively removed.

III. CRYSTAL DATA

The crystals of GaP(Cd,O) and GaP(Zn,O) were grown by cooling Ga-rich solutions in sealed evacuated vitreous silica tubes.[10] The acceptor concentration was varied by changing the percentage of acceptor added to the melt. The oxygen content was varied by adding Ga_2O_3 to the melt. Invariably oxygen is also present as a natural impurity in the starting materials, so that the total oxygen concentration is incompletely controlled. Although the distribution coefficient for Cd between Ga and GaP is unknown, the solubility of Cd is much smaller than Zn in GaP. Barrier capacitance measurements show that the amount of Cd was not greatly in excess of the donor contaminants; sulphur is the major inadvertant donor impurity.

When the Cd-doped crystals were slowly cooled to room temperature after growth, bound-exciton decay

---

[9] J. D. Cuthbert and D. G. Thomas, J. Appl. Phys. **39**, 1573 (1968).

[10] See, for example, J. F. Miller, in *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold Publishing Corp., New York, 1962), Vol. 1, Chap. 23.

dominated the low-temperature red luminescence. On the other hand, when the Cd-doped samples were rapidly cooled after growth from 800°C to room temperature, the pair recombination dominated the red luminescence. It is believed that slow cooling reduces the number of isolated Cd acceptors. At present the fate of these acceptors is uncertain. It might be theorized that this reduction in the acceptor concentration results from an increased pairing with O donors, but absorption measurements did not confirm this. Decreasing the number of Cd acceptors decreases the pair luminescence relative to the bound-exciton luminescence. Although observable, these effects are less prominent in Zn-doped samples, especially at high acceptor concentration, probably because Zn is much more soluble in the GaP lattice than Cd.

IV. RESULTS

A. Bound-Exciton Decay Times in GaP(Cd,O) and GaP(Zn,O)

The decay time of the bound exciton was studied in several slow-cooled crystals of GaP(Cd,O). Slow cooling emphasizes the bound-exciton band relative to the pair band. Further discrimination against the pair band was obtained by choosing a spectrometer wavelength setting corresponding to the prominent zero-phonon line or first-phonon replica. Figure 2 shows that the decays are exponential and have values of 560 and 330 nsec at 1.7 and 20°K, respectively. Many of the crystals showed a small post-excitation increase in luminescence lasting about 15 nsec. The luminescence efficiency remains constant in this temperature interval, so it is concluded that the change in decay time results from thermalization between the bound-exciton *A* and *B* states[1] which are separated by an energy of 2.1 meV. A straightforward calculation based on these experimental values and Eq. (1) in Ref. 11 yields the decay time values $\tau_A=0.1$ μsec and $\tau_B=0.6$ μsec.

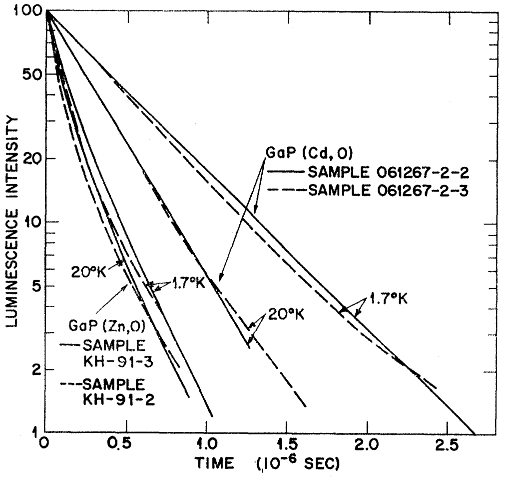

FIG. 2. Fluorescence time-decay characteristics for two slow-cooled crystals of GaP(Cd,O) and GaP(Zn,O). For GaP(Cd,O) the zero of time is taken 15 nsec after the end of the exciting electron pulse. For GaP(Zn,O) the zero of time is at the end of the exciting pulse.

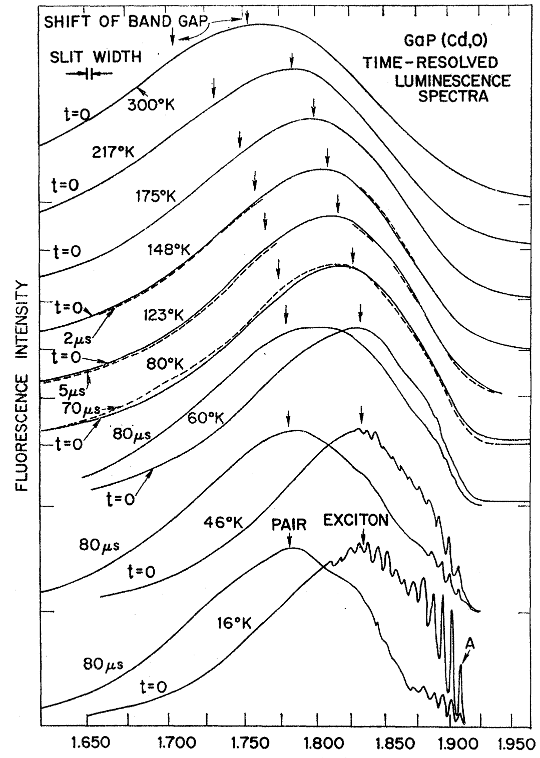

FIG. 3. Normalized time-resolved spectra as a function of the temperature of a fast-cooled crystal of GaP(Cd,O). The exciting electron beam current density was about 0.05 A/cm^2. At 16°K the arrows show the energies of the peaks of the clearly resolved pair and bound-exciton bands. The arrows at higher temperatures show the expected energy position of these peaks after the variation in band-gap energy is allowed for.

For GaP(Zn,O) it is not possible to discriminate spectrally against the pair decay because of the overlap of the pair and bound-exciton bands and because of the absence of sharp lines in the latter. Slow-cooled, rather strongly excited crystals afford the best chance of observing the true excitonic decay time. Under such conditions the density of exciton-hole states is high, thereby enhancing the bound-exciton band.

Figure 2 shows that the decays at 1.7 and 20°K are similar and reasonably exponential. No post-excitation increase in luminescence occurred in these crystals. Assuming that the *j-j* splitting of the *A* and *B* states is roughly equal to that in GaP(Cd,O), the lack of any temperature dependence due to thermalization between the *A* and *B* states implies a large degree of mixing between these states. The data indicate a value for τ_A of about 100 nsec.

For both GaP(Cd,O) and GaP(Zn,O) the slight sample dependence of the time-decay characteristics is

---

[11] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

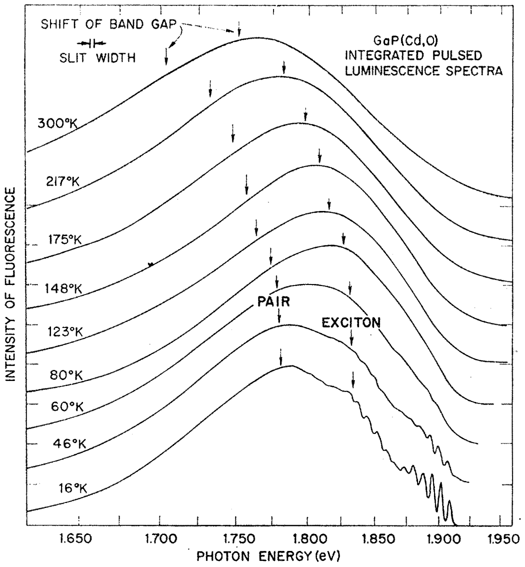

FIG. 4. Normalized spectra obtained by integrating the photomultiplier response to the light from the same pulse-excited crystal of GaP(Cd,O) used for Fig. 3. The excitation conditions were identical with those in Fig. 3. The arrows show the expected energy positions of the bound-exciton and pair-band peaks at the various temperatures. Up to about 60°K the pair band is dominant. Above the transitional temperature range (approximately 70–100°K), the bound-exciton band dominates.

attributed to the variable contribution of the long-lived pair luminescence.

B. Temperature Dependence of Luminescence Decay Curves and Time-Resolved Spectra for GaP(Cd,O)

Figure 3 shows the temperature dependence of the time-resolved spectra from a fast-cooled sample of GaP(Cd,O). It may be assumed that the bands have the same change in energy with temperature as the indirect band gap. According to this assumption, the arrows in the figure indicate where the peaks of the bound-exciton band and pair band would be expected to lie at high temperatures. As explained in the previous section, fast-cooled crystals have a larger fraction of pair luminescence which was desirable here. At temperatures up to 46°K the pair and bound-exciton bands are clearly resolved. At 60°K the bound-exciton band appears almost unchanged in energy although the sharp phonon sidebands have become thermally broadened to the extent that they are almost unresolved. The pair peak however has shifted distinctly to higher energy. Between 60 and 80°K the two bands have merged into a single spectrum located at an intermediate energy. Between 80 and 148°K the spectrum moves to higher energy relative to the band gap until it coincides with the position predicted for the bound-exciton band alone.

The relative contributions of the bound-exciton and pair bands to the total luminescence can be inferred from Fig. 4, which shows the spectra formed by in-

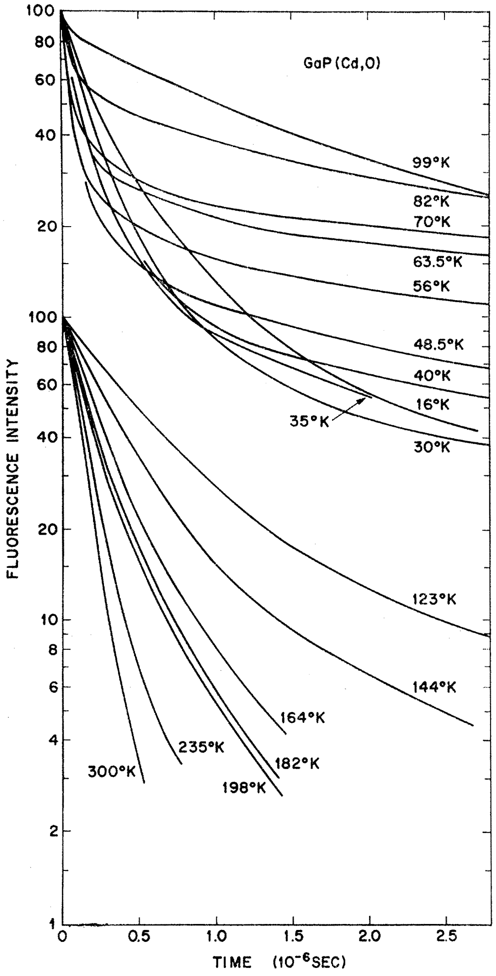

FIG. 5. Total luminescence time-decay characteristics of the red band from the same GaP(Cd,O) crystal and with the same excitations used for Fig. 3. At low temperatures the decays show the fast exciton decay followed by the long pair decay. Between 80 and 100°K the bound-exciton decay lengthens and merges with the long-lived component. Above 100°K the decay rate increases and becomes more nearly exponential.

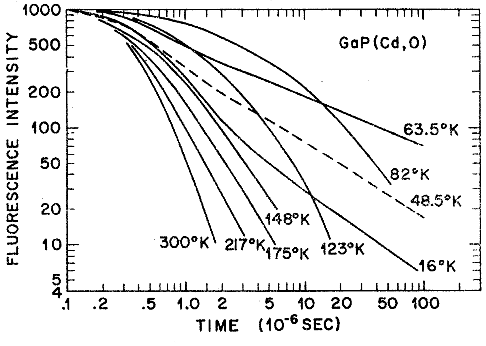

FIG. 6. Total time-decay characteristics of the long-lived luminescence from the same GaP(Cd,O) crystal and with the same excitation conditions used for Fig. 3. At temperatures up to 63°K the long-lived luminescence obeys a power-law characteristic of pair decay. At 83°K and above, the decay rate of the long-lived luminescence increases rapidly.

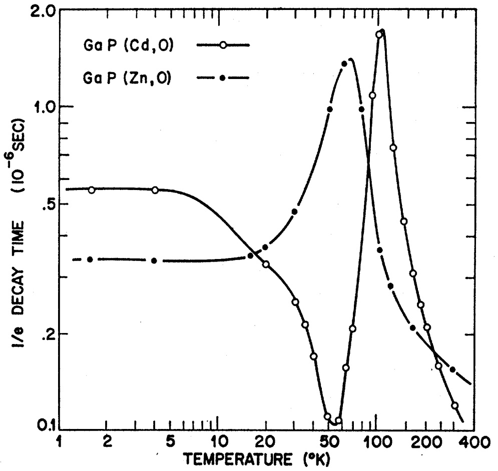

FIG. 7. Plots of the $1/e$ decay times ($\tau_{1/e}$) taken from Figs. 5 and 10. For GaP(Cd,O) the initial decrease in $\tau_{1/e}$ is caused by the thermal redistribution of the bound-exciton population between the A and B exciton states. The changes in $\tau_{1/e}$ at temperatures above 60°K are due to the onset of thermal equilibrium of holes among the hole states. A similar situation holds for GaP(Zn,O) although, for reasons discussed in the text, no initial decrease in $\tau_{1/e}$ is observed.

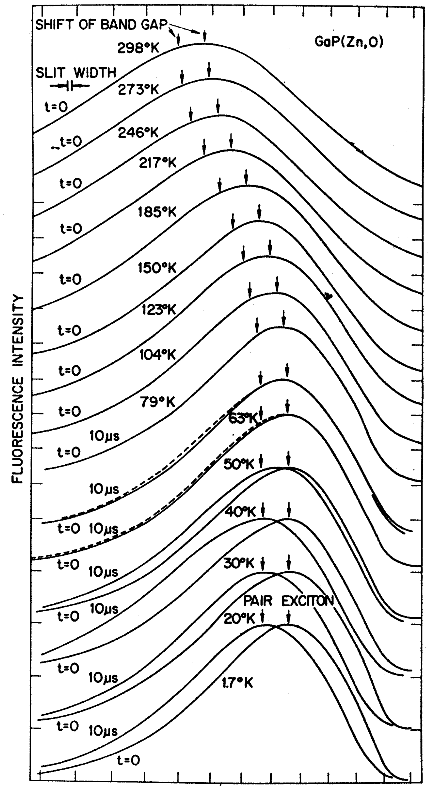

FIG. 8. Normalized time-resolved spectra as a function of the temperature of a fast-cooled crystal of GaP(Zn,O). The exciting electron beam current density was about 0.05 A/cm². At 1.7°K the arrows show the peaks of the resolved pair and bound-exciton bands. The arrows at higher temperatures show the expected energy position of these peaks after allowing for the variation in band-gap energy.

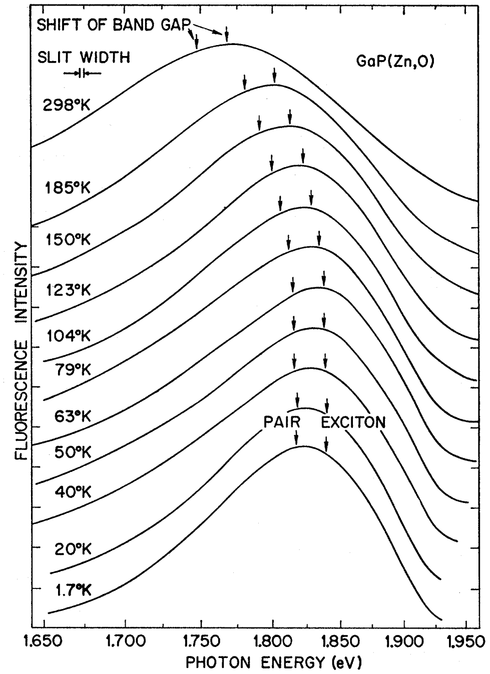

FIG. 9. Normalized spectra obtained by integrating the photomultiplier response to the light from the same pulse-excited crystal of GaP(Cd,O) and with the same excitation conditions used for Fig. 8. The arrows show the expected energy positions of the bound-exciton and pair-band peaks at the various temperatures.

tegrating the single pulses from the photomultiplier. A careful comparison of the normalized spectra in Figs. 3 and 4 shows that up to approximately 80°K, where the time-resolved spectra coalesce, the integrated and pair bands are identical. Above 80°K the spectra in the two figures must be, and are, identical, and correspond mainly to bound-exciton recombination. The total red-luminescence efficiency was found to change with temperature in much the same way as previously reported for GaP(Zn,O).[4]

The time-decay characteristics of the total red emission as a function of temperature for the same crystal are presented in Figs. 5 and 6 for the time ranges 0–2.8 μsec and 0.1–100 μsec, respectively. At all temperatures it was noticed that the buildup time of the luminescence was equal to the length (100 nsec) of the exciting pulse (cf. Ref. 6). It is seen in Fig. 5 that up to about 70°K there is an initial fast decaying luminescence followed by a very long-lived component, which, considering the results in Fig. 3, must be associated with the bound-exciton and pair luminescence bands, respectively. The $1/e$ decay times $\tau_{1/e}$ taken from Fig. 5 are plotted in Fig. 7. Thermalization of excitons from the B into the A state causes the temporary decline in $\tau_{1/e}$ as the temperature is raised from 1.7°K (See Sec. IV A). Figure 5 shows that between 70 and 90°K the pure bound-exciton component becomes much less noticeable; Fig. 6 shows that in this same temperature

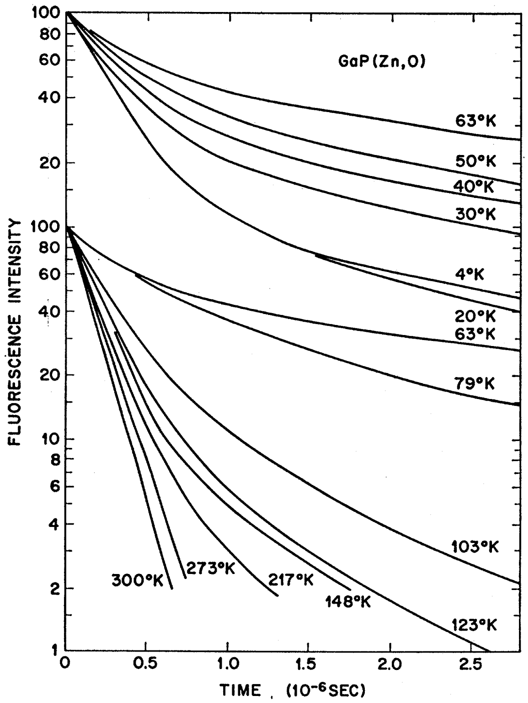

FIG. 10. Total luminescence time-decay characteristics of the red band from the same crystal and with the same excitation conditions used for Fig. 8.

range, the long-lived luminescence begins to decay much faster. These results corroborate the results in Figs. 3 and 4 by showing that near 70°K the pair and bound-exciton systems have a similar time decay. As the temperature is increased beyond this point, the luminescence decay rate gets progressively faster and becomes more nearly exponential in form. These changes are clearly reflected by the parameter $\tau_{1/e}$ in Fig. 7.

In the temperature range ($\lesssim 50°$K) where thermal equilibrium is not attained, it is observed that the intensity of the bound-exciton band increases rapidly relative to the pair band for exciting beam current densities in the range 0.01–0.1 A/cm^2, corresponding to carrier injections of 10^{16}–10^{17} electron-hole pairs/cm^3 per pulse. In terms of the model for the luminescence, this variation is reasonable, since the density of exciton-hole states is always equal to the number of occupied Cd-O$^-$ states and the latter is proportional to pumping power. Hence, low pumping intensity ($<10^{16}$ electron-hole pair/cm^3) favors pair recombination because the density of exciton-hole states is small in comparison to the density of free cadmium acceptor states, estimated to be $\sim 10^{17}$/cm^3. When the carrier injection per pulse is approximately equal to this acceptor density, the probability for the capture of holes into the isolated acceptor and exciton-hole states will be comparable and the bound-exciton band will grow relative to the pair band.

C. Temperature Dependence of Luminescence Decay Curves and Time-Resolved Spectra for GaP(Zn,O)

The temperature dependence of the time-resolved spectra for GaP(Zn,O), shown in Fig. 8, is qualitatively the same as that in Fig. 3 for GaP(Cd,O). For this crystal there is little change in the spectra up to 30°K. At 40°K the pair band has moved significantly to higher energies, whereas the bound-exciton band has hardly changed in position. By 60°K it has become impossible to distinguish the individual emissions through time-resolved spectroscopy; this indicates that the two bands now have similar time decays. At this temperature the location of the composite band is slightly shifted to lower energies from the position that the bound-exciton band alone would occupy. From 60 to 100°K, the composite band shifts a little further to higher energies relative to the band-gap energy to become coincident with the exciton band. At still higher temperatures the shifts are accounted for by band-gap variation alone.

Figure 9 shows the integrated spectra for the same excitation intensity and temperatures. Detailed comparison of the spectra in Figs. 8 and 9 shows that the integrated spectra fall nearer the 10-μsec time-resolved pair spectra at temperatures up to 30°K. At higher temperatures the emission becomes progressively more heavily weighted towards bound-exciton emission. The total red-luminescence intensity altered with temperature in the way previously described.[4]

Figures 10 and 11 show the corresponding temperature dependence of the luminescence time-decay characteristics of the total red emission for the same crystal. The $\tau_{1/e}$ decay times are plotted versus temperature in Fig. 7. Comparison with GaP(Cd,O) in the low-temperature region up to 30°K shows the initial fast

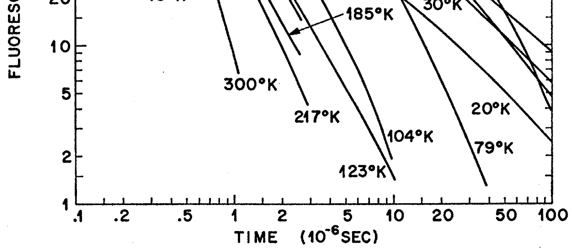

FIG. 11. Total time-decay characteristics of the long-lived luminescence from the same GaP(Zn,O) crystal and with the same excitation conditions used for Fig. 8.

decay due to the bound-exciton is not as easily distinguished from the slow decay of the pairs in this crystal. However, other crystals were examined in which the bound exciton was very dominant at the lowest temperatures, and in such cases the faster decaying bound exciton was readily distinguished. Nevertheless, it is easily seen from Figs. 7 and 10 that as the temperature is raised to about 60°K the initial excitonic decay becomes increasingly long, after which it decreases. Note that in agreement with the results of Sec. IV A an initial decrease in $\tau_{1/e}$, due to excitons thermalizing from the B state into the A state as the temperature is raised above 1.7°K, is not observed for GaP(Zn,O).

The decay rate of the luminescence at longer times due to the pairs (Fig. 11) exhibits little change with temperature up to 50°K. Between 60 and 100°K the decay rate of the long-lived component increases very rapidly and at still higher temperatures continues to increase but more slowly. This behavior is consistent with the data in Figs. 8 and 9, which show a sizable contribution from pair emission up to about 60°K and an increasingly dominant bound-exciton emission above the transitional temperature range 50–70°K.

Some evidence of low-temperature tunneling between hole states was obtained from a series of experiments in which an argon ion laser was used to excite GaP(Zn,O) crystals containing Zn concentrations in the range from 2×10^{17} to 5×10^{18} atoms/cm^3 at 1.7°K. When the argon ion laser was focused, the bound-exciton band dominated the emission for all crystals. In the unfocused condition (pumping intensity down by a factor of 10^{-4}), the pair band was dominant at Zn concentrations in the range from 2 to 5×10^{17} atoms/cm^3, while for higher concentrations the bound-exciton-band intensity increased with concentration. This result is attributed to an increased probability of tunneling between hole states at high acceptor concentrations.

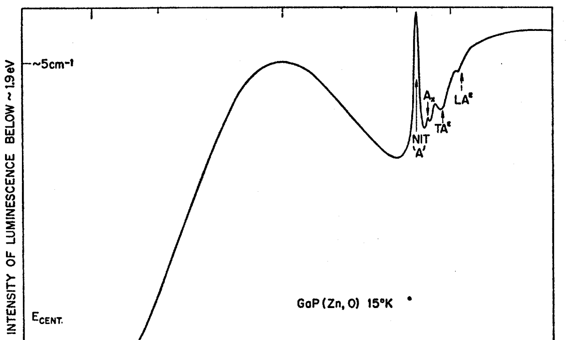

FIG. 12. Luminescence excitation spectrum for a slow-cooled crystal of GaP(Zn,O).

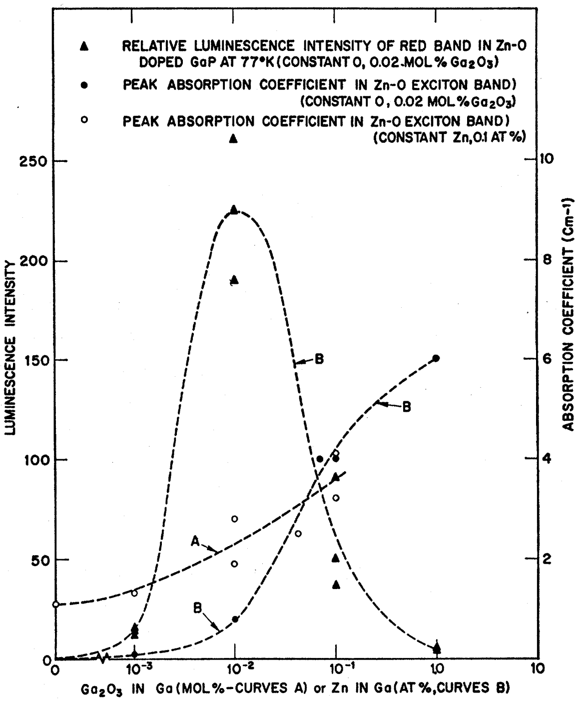

FIG. 13. Dependence of the relative red-luminescence intensity and of the peak absorption coefficient in the Zn-O exciton band on the melt composition.

D. Exciton Absorption Spectra of Cd-O and Zn-O Complexes

The exact shapes of the absorption bands due to the creation of excitons bound to nearest-neighbor donor-acceptor pair complexes were difficult to determine by direct means, since the bands are very broad and the absorption is weak. The absorption spectra were more conveniently obtained from measurements of the intensity of the bound-exciton luminescence as the energy of the exciting radiation, corrected to constant excitation intensity, was scanned through the absorption bands. These spectra will be called LE (luminescence excitation) absorption spectra.

The low temperature Cd-O LE absorption spectrum obtained in this way is considerably broader than the bound-exciton luminescence spectrum, and the phonon structure is much weaker.[12] The Zn-O exciton luminescence spectrum is almost devoid of structure, so it is not surprising that the corresponding LE absorption spectrum shown in Fig. 12 is broad and quite featureless. The no-phonon transition energy of excitons decaying at Zn-O complexes is located near the arrow labeled E_{cent} at 2.01 eV, a point midway between the low-energy half-maximum of the LE absorption spec-

---

[12] C. H. Henry, P. J. Dean, D. G. Thomas, and J. J. Hopfield, in Proceedings of the International Conference on Localized Excitations in Solids, Irvine, California, 1967 (to be published).

trum and the high-energy half-maximum of the luminescence spectrum.[13]

The absorption scale in Fig. 12 is relevant only to the Zn-O absorption band below 2.30 eV. The structure above this energy is due to the photocreation of excitons at isoelectronic nitrogen impurities (lines A and A_x [14]) and to intrinsic absorption processes (indirect absorption threshold TA^E and LA^E [15]). These absorption processes contribute relatively weakly to the Zn-O exciton luminescence and are therefore lightly weighted in the LE absorption spectrum. The peak absorption of the Zn-O exciton band is $\sim 5\ \mathrm{cm}^{-1}$ in GaP crystals optimally doped for the red luminescence measured at 80 or 300°K, shown in this paper to be due mainly to Zn-O exciton recombinations. When we use the oscillator strength $f \sim 0.07$ of the Zn-O exciton transition derived from the decay-time measurements of the luminescence, the absorption coefficient corresponds to a Zn-O concentration of $\sim 5\times 10^{16}$ atoms/cm^3.

It has previously been reported that maximum red luminescence is obtained in solution-grown crystals from Ga containing 0.1 at.% Zn and 0.01 at.% $\mathrm{Ga_2O_3}$.[4] Figure 13 shows that for the series of crystals examined in the present work, the red-fluorescence intensity was a maximum for Ga solutions containing close to 0.01 at.% Zn. The concentrations of free Zn acceptors in crystals grown from Ga solution containing, respectively, 0.01, 0.1, and 1 at.% Zn are 0.5, 1.5, and 5×10^{18} atoms/cm^3. It is interesting to note that the Zn-O exciton absorption of these crystals continues to increase up to 1 at.% Zn-doped Ga solution although the luminescence efficiency falls rapidly in this region. It has been shown recently[16] that Auger recombination causes a rapid decrease in the low-temperature luminescence efficiency of the relatively tightly bound bismuth-exciton transition in GaP above a neutral donor concentration of $\sim 10^{18}/\mathrm{cm}^3$. Impurity banding sets in at this donor concentration and promotes the interaction of a third electronic particle with the bound exciton. It is very likely that a similar effect is responsible for the quenching of the Zn-O bound-exciton luminescence at the higher Zn concentrations, shown in Fig. 13. According to this model the onset of concentration quenching is expected to be insensitive to temperature changes in the range where isolated Zn acceptors become thermally unstable, in agreement with experiment.

Figure 13 also shows that the Zn-O exciton absorption increases with the amount of $\mathrm{Ga_2O_3}$ in the Ga solution. While there is no background of Zn, there is a significant background concentration of O in these crystals. Recent experiments[3] using the O^{18} isotope shift of the Cd-O bound-exciton no-phonon line as an indicator have shown that it is very difficult to obtain an increase in the concentration of these complexes greater than a factor of 4 or 5. The residual concentration of Cd-O sites is about $0.5\times 10^{+16}/\mathrm{cm}^3$ in slow-cooled crystals grown in sealed-off quartz tubes from Ga solution containing 10 at.% Cd, even when rigorous measures are taken to exclude O. Possible sources of this O are the quartz tubes and the GaP source material.

V. DISCUSSION

The time-resolved spectra and luminescence time-decay characteristics of the red luminescence exhibit the following principle features.

(a) At low temperatures there is a rapid bound-exciton decay followed by a slow pair decay and two distinct spectra are recorded in time-resolved spectroscopy corresponding to the pair and bound-exciton bands. The crystals chosen for the study had prominent pair bands at low temperatures at the excitation levels used.

(b) As the temperature is raised above about 60°K for GaP(Zn,O) and about 80°K for GaP(Cd,O) the initial fast excitonic component in the total time decay lengthens to become substantially longer than the bound-exciton lifetime. Also, the long pair decay shortens, so that the combined time-decay characteristics eventually approximate a single exponential. At the same time, the intensity spectra alter and show that the bound-exciton band begins to dominate the total emission.

(c) As the temperature is raised still further, the time-decay characteristics of the total luminescence get significantly more rapid. Apart from broadening and a shift due to the band-gap variation with temperature, no further changes in the intensity spectra are seen.

These effects can be accounted for semiquantitatively by assuming that the holes in acceptor states, in bound-exciton hole states, and in the valence band are in thermal equilibrium at the higher temperatures. It is also assumed that in the temperature range 1.7–300°K the electron remains trapped at the acceptor oxygen complex. Let p_{A} and p_{ex} be the occupation probabilities for a hole to be in an acceptor state and in a bound-exciton hole state. If the holes are in thermal equilibrium, the occupation probabilities are given by Fermi-Dirac statistics as [17]

$$p_{\mathrm{A}}=[1+D_{\mathrm{A}}^{-1}\exp\{(E_{\mathrm{F}}-E_{\mathrm{A}})/kT\}]^{-1}, \qquad (1)$$

$$p_{\mathrm{ex}}=[1+D_{\mathrm{ex}}^{-1}\exp\{(E_{\mathrm{F}}-E_{\mathrm{ex}})/kT\}]^{-1}, \qquad (2)$$

where E_{F}, E_{A}, and E_{ex} are the energies of the quasi-

---

[13] The exact relationship between E_{cent} and the no-phonon transition energy of the Zn-O exciton is unknown, but the latter probably lies a little below the former since the half-bandwidths of the two spectra suggest that the Huang-Phys factor is larger in the absorption spectrum.

[14] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[15] P. J. Dean and D. G. Thomas, Phys. Rev. **150**, 690 (1966).

[16] J. C. Tsang, P. J. Dean, and P. T. Landsberg (to be published).

[17] See, for example, J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962).

Fermi level governing the hole distribution, the acceptor level, and the level corresponding to a hole in a bound-exciton hole state. These energies are measured relative to the valence-band maximum. D_A and D_{ex} are the degeneracies of the hole on the acceptor and in the bound exciton. The acceptor ground state is fourfold degenerate, while the hole in the bound exciton is twofold degenerate.[18] Let τ be the lifetime of an electron trapped on the acceptor-oxygen complex. The trapped electron decay rate τ^{-1} is given by

$$\tau^{-1}=W_{ex}p_{ex}+\sum_r W(r)p_A\,, \tag{3}$$

where W_{ex} is the exciton decay rate and $W(r)$ is the decay rate for the electron to recombine with a hole located on an acceptor a distance r from the trapped electron. The transition rate $W(r)$ is taken to be[19]

$$W(r)=W_{max}\exp(-2r/a)\,, \tag{4}$$

where a is the Bohr radius of the hole on the shallow acceptor. This formula is only valid when either the hole or the electron is tightly bound. It is applicable in our situation because the electron is very tightly bound compared to the hole. W_{max} is the transition rate for $r=0$ (that is, when the electron and hole wave functions have maximum overlap). W_{max} is estimated to be equal to W_{ex} multiplied by the ratio of the maximum hole density on the acceptor to the maximum hole density in the bound exciton. These densities are inversely proportional to the cube of the ratio of the Bohr radii of the holes on the acceptor (a) and in the bound exciton (a_{ex}) so that

$$W_{max}\approx W_{ex}(a_{ex}/a)^3\,. \tag{5}$$

The total rate of pair decay is given by

$$\sum_r W(r)=(N_A-N_D)W_{ex}(a_{ex}/a)^3\int_0^\infty 4\pi r^2 \times\exp(-2r/a)\,dr=(N_A-N_D)W_{ex}a_{ex}{}^3\pi\,, \tag{6}$$

where N_A is the acceptor density, N_D is the donor density, and (N_A-N_D) is the density of neutral acceptors. The ratio of the bound-exciton intensity to the pair-band intensity is given by

$$I_{ex}/I_{pair}=W_{ex}p_{ex}/\sum_r W(r)p_A \approx p_{ex}/p_A(N_A-N_D)a_{ex}{}^3\pi\,. \tag{7}$$

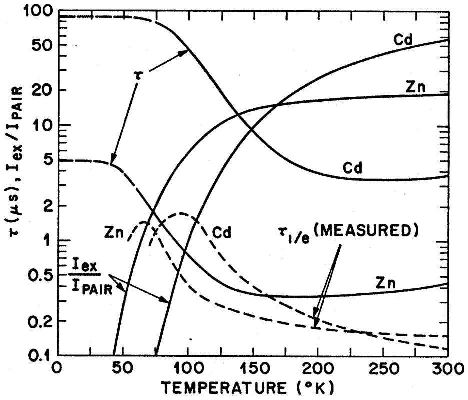

FIG. 14. Comparison of the calculated decay times with the experimentally determined decay times of the red emission. A comparison is only meaningful at temperatures where thermal equilibrium conditions approximate, namely, above ~80°K for GaP(Cd,O) and ~60°K for GaP(Zn,O).

The Boltzmann factors appearing in Eqs. (1) and (2) may be calculated using standard semiconductor statistics.[17] They depend upon N_A, N_D, the binding energy of the acceptor E_A, and the density of states effective mass of the hole, which is taken to be 0.37 times the free electron mass.[20]

For the case of GaP(Zn,O), we take $N_A=10^{18}$ atoms/cm^3 and $N_D=2\times10^{17}$ atoms/cm^3. The binding energy of the Zn acceptor is known to be 62 meV.[21] These estimates of N_A and N_D for the Zn-doped samples are based on the solubility measurements of Trumbore *et al.*[22] The Cd-doped samples are less heavily doped and more highly compensated than the Zn-doped samples, and we estimate that $N_A=10^{17}$ atoms/cm^3 and $N_D=4\times10^{16}$ atoms/cm^3. We are much less certain of the latter parameters than of the parameters for the Zn-doped samples. The binding energy of the Cd acceptor is known to be 95 meV.[21] For both Zn and Cd we take W_{ex} to be 10^7 sec^{-1} (see Sec. IV A), the binding energy of the hole in the bound exciton to be 36 meV, and the Bohr radius of the hole in the bound exciton to be 16.9 Å. The predicted lifetime τ and ratio I_{ex}/I_{pair} are plotted versus temperature in Fig. 14.

If true thermal equilibrium were achieved, the red luminescence would decay exponentially, giving straight lines in Figs. 5 and 10. The deviation from an exponential decay gives some indication of the deviation from thermal equilibrium. Clearly, at low temperatures there is very little thermalization. Because thermal equilibrium is only approximately achieved even at the higher temperatures, only qualitative agreement is expected between theory and experiment.

---

[18] The zone center valence band hole states are fourfold degenerate. These states are split into two Kramers doublets by the crystal field of the acceptor-oxygen site. (See Refs. 1 and 12.) In calculating p_{ex} we should take into account both doublets; this is done by changing D_{ex} in Eq. (2) from 2 to $2+2\exp(-\Delta E/kT)$, where ΔE is the splitting between the states and is taken to be 10 meV. We cannot justify this choice, but other reasonable values of ΔE would not substantially alter the results of the calculation.

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

[20] R. A. Faulkner (private communication).

[21] P. J. Dean, J. P. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **18**, 122 (1967).

[22] F. A. Trumbore, H. G. White, M. Kowalchik, R. A. Logan, and C. L. Luke, J. Electrochem. Soc. **112**, 782 (1965).

The ratio I_{ex}/I_{pair} is predicted to be unity at 65°K for the Zn-doped sample and at 100°K for the Cd-doped sample and to increase rapidly with temperature. Experimentally, it is found that the bound exciton becomes dominant above 60°K in Zn-doped samples and above 80°K in Cd-doped samples in good agreement with theory. It is predicted that the ratios of I_{ex}/I_{pair} are 19 for Zn-doped samples and 57 for Cd-doped samples at 300°K.

At room temperature the densities of free holes in the valence band and holes in the acceptor states are of the same order of magnitude, so that the intensity of the recombination luminescence due to free holes annihilating the trapped electrons is expected to be of the same order of magnitude as the pair-luminescence intensity. Therefore, the bound-exciton luminescence is predicted to dominate both the pair luminescence and the free-to-bound luminescence at room temperature, in agreement with experiment.

The calculated and measured lifetimes are compared in Fig. 14. The experimental lifetimes peak at 65°K in Zn-doped crystals and at 95°K in Cd-doped crystals. Theory and experiment can only be compared at these temperatures and at higher temperatures. Below these temperatures little thermalization of the holes has taken place. The agreement between theory and experiment is fairly good for the case of GaP(Zn,O). The maximum experimental lifetime $\tau_{1/e}$ (measured at the e^{-1} intensity point) is 1.5 μsec at 65°K. The predicted value at this temperature is 2.3 μsec. At higher temperatures both the predicted and the experimental lifetimes decrease. The experimental lifetime decreases faster, however, presumably because nonradiative processes shorten the experimental lifetime and these processes become increasingly important at higher temperatures.

For the Cd-doped crystals, the agreement is much worse. While the experimental lifetime at 100°K of 1.7 μsec is long compared with the exciton lifetime (0.1 μsec), in agreement with our ideas, this lifetime is small compared with the predicted lifetime of 45 μsec. The agreement remains poor at higher temperatures. At present the reason for this disagreement is not understood. It may result because thermalization is less likely in Cd-doped samples because of the large Cd binding energy (95 meV) and because the assumed concentration of Cd acceptors is rather low. It is also possible that nonradiative processes, which shorten the measured lifetime, are more important in the Cd-doped material.

VI. CONCLUSIONS

It was previously established by Henry, Dean, and Cuthbert[1] that the low-temperature red luminescence in GaP(Zn,O) and GaP(Cd,O) is due to the near superposition of a pair band and a bound-exciton band. In this paper, the red luminescence has been studied by electron beam excitation in the temperature range 1.7–300°K. Above about 50°K the bound holes in the acceptor and exciton-hole states tend to come into thermal equilibrium. The thermalization appears to be only partially achieved, becoming more effective at higher temperatures. The result of this thermalization is to cause the red luminescence to be dominated by bound-exciton decay above 60°K in Zn-doped crystals and above 80°K in Cd-doped crystals. As thermalization is achieved, the time-decay characteristic of the red luminescence becomes more nearly exponential. Although the red luminescence is dominated by bound-exciton decay above 80°K, the decay time of the luminescence is much longer than the bound-exciton decay time between 80 and 150°K, because the processes promoting thermal equilibrium cause holes to be continuously transferred from the acceptor into the bound-exciton hole states. The decay time becomes shorter with increasing temperature as the bound-exciton decay becomes increasingly dominant. Bound-exciton decay is the principal source of red luminescence at room temperature. These results can be explained semiquantitatively by the theory of thermal equilibrium among the hole states presented in this paper. The agreement between theory and experiment is much better for Zn than for Cd. Measurement of the luminescence excitation spectra in GaP(Zn,O) shows that although the concentration of Zn-O complexes continues to rise as the Zn acceptor concentration is increased above that corresponding to maximum luminescence efficiency, the onset of concentration quenching of the luminescence, probably by nonradiative Auger processes, offests any possible increase in luminescence efficiency. The absolute concentrations of the Zn-O and Cd-O complexes have been estimated from measurements of the exciton absorptions and luminescence decay times.

ACKNOWLEDGMENTS

The authors are indebted to R. T. Lynch for the crystals and to W. P. Knox for constructing the variable-temperature irradiation Dewar. Discussions with R. A. Faulkner, D. G. Thomas, and D. K. Wilson were most helpful and encouraging.