

Radiative Pair Transitions in *p*-Type ZnSe:Cu Crystals\*

GERALD B. STRINGFELLOW† AND RICHARD H. BUBE

*Department of Materials Science, Stanford University, Stanford, California*

(Received 5 February 1968; in final form 8 March 1968)

Shallow levels with an ionization energy of 0.012 eV play an important role in the photoelectronic properties of *p*-type ZnSe:Cu crystals. These levels exhibit the characteristics of the higher-lying member of an imperfection pair involved in luminescence emission, as well as of a trap determining long-time decay rates of luminescence and photoconductivity, and of a center causing low-temperature reduction of free-electron lifetime. The participation of the shallow level in low-temperature pair emission is demonstrated by the thermal quenching of the emission at 50°K with an activation energy of 0.012 eV, whereas the acceptor forming the lower-lying member of the pair lies 0.72 eV above the valence band, and by the shift in the position of the emission band below 50°K with changing excitation intensity. The energetics of the emission and the  $10^{-20}$  cm<sup>2</sup> electron cross section determined from decay suggest that the shallow level may be an acceptor rather than a donor.

## INTRODUCTION

Several broad luminescence bands are found in II-VI compounds, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, containing copper impurity. Many different models have been proposed for the physical mechanism of the luminescence transitions. These include the Klasens-Schön model<sup>1,2</sup> involving capture of a free electron by a bound hole, the Lambe-Klick<sup>3</sup> model involving capture of a free hole by a bound electron, and the Prener-Williams<sup>4,5</sup> model involving recombination between an electron captured at a donor with a hole captured at a nearby acceptor. The Prener-Williams model was based on the experimental evidence that <sup>65</sup>Zn decaying to <sup>65</sup>Cu in ZnS did not produce the green emission characteristic of ZnS containing copper acceptors and chlorine donors.<sup>6-8</sup> Other indirect evidence has been presented to support a model involving associated or unassociated pair transitions in II-VI compounds, such as time-resolved spectra of the broad bands.<sup>9</sup> An investigation of copper luminescence in ZnS crystals indicated that many of the features characteristic of such pair emission were absent,<sup>10</sup> and that it was likely that the cop-

per-chlorine luminescence center could be adequately described in terms of transitions from the conduction band to a single level.

The existence of donor-acceptor pair emission was established in GaP<sup>11-13</sup> where an emission spectrum consisting of a series of sharp lines converging into a continuum at low energies was found. Each line could be identified as due to transitions between donors and acceptors with a particular spatial separation. For separations of more than 40 Å, the discrete lines merge into a broad band. The position and shape of the broad band depends on the energies of donor and acceptor, on the excitation intensity, and on time during decay of the emission. This recombination mechanism is highly efficient at low temperatures, but as the temperature is raised, thermal ionization of the shallower member of the participating pair decreases the efficiency. Strong thermal quenching occurs in the reported cases in GaP at or below 100°K. It was the absence of such thermal quenching in the case of the green emission of copper in ZnS that argued against the unassociated pair model for that system.<sup>10</sup>

It is the purpose of the present paper to present evidence that the low-temperature red (1.95 eV) emission due to copper acceptors in *p*-type ZnSe:Cu is due to a pair recombination mechanism. The levels involved are a shallow level lying 0.012 eV below the conduction band, and the empty Cu<sub>Zn</sub>' level, lying 0.72 eV above the valence band. The shallow 0.012-eV levels also manifest their presence in affecting other photoelectronic processes: determining long-time decay rates for all luminescence emissions and for photoconductivity, and acting to reduce the free-electron lifetime below 50°K.

A summary of the conclusions about the nature of copper impurity in ZnSe:Cu crystals has previously

\* Supported partially by the U.S. Army Research Office (Durham), partially by the U.S. Army Engineers Research and Development Laboratories, Fort Belvoir, and partially by the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

† Present address: Hewlett-Packard Laboratories, Palo Alto, Calif.

<sup>1</sup> M. Schön, *Z. Physik* **119**, 463 (1942).

<sup>2</sup> H. A. Klasens, *Nature* **158**, 306 (1946).

<sup>3</sup> J. Lambe and C. C. Klick, *Phys. Rev.* **98**, 909 (1955).

<sup>4</sup> E. F. Apple and F. Williams, *J. Electrochem. Soc.* **106**, 224 (1959).

<sup>5</sup> J. S. Prener and D. J. Weil, *J. Electrochem. Soc.* **106**, 409 (1959).

<sup>6</sup> J. S. Prener and F. E. Williams, *J. Electrochem. Soc.* **103**, 342 (1956).

<sup>7</sup> R. M. Potter, M. Aven, and J. Kastner, *J. Electrochem. Soc.* **109**, 1154 (1962).

<sup>8</sup> I. Broser and K. H. Franke, *J. Phys. Chem. Solids* **26**, 1013 (1965).

<sup>9</sup> S. Shionoya, K. Era, and Y. Washizawa, *J. Phys. Soc. Japan* **21**, 1624 (1966).

<sup>10</sup> C. S. Kang, P. B. P. Phipps, and R. H. Bube, *Phys. Rev.* **156**, 998 (1967).

<sup>11</sup> J. J. Hopfield, D. G. Thomas, and M. Gershenson, *Phys. Rev. Letters* **10**, 162 (1964).

<sup>12</sup> D. G. Thomas, M. Gershenson, and F. A. Trumbore, *Phys. Rev.* **133**, A269 (1964).

<sup>13</sup> M. Gershenson, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, *J. Appl. Phys.* **36**, 1528 (1965); *J. Appl. Phys.* **37**, 483 (1966); *ibid.* 486 (1966).

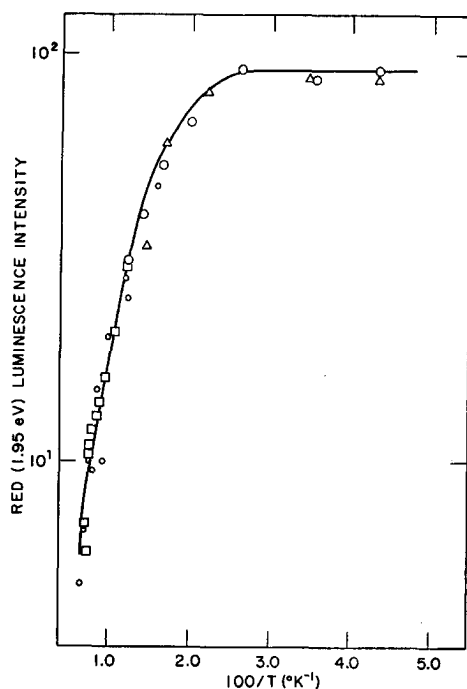


FIG. 1. Temperature dependence of the 1.95-eV red emission.

been published.<sup>14</sup> The details of the photoelectronic properties of ZnSe:Cu, to which reference is made in the present paper for supporting data, as well as a description of crystal preparation and measurement techniques, are given in a separate publication.<sup>15</sup>

## RESULTS AND DISCUSSION

### General Properties of the *p*-Type ZnSe:Cu Crystals<sup>15</sup>

The crystals involved in this study were low-conductivity *p*-type, with the Fermi level at room temperature lying 0.69 eV above the valence band. The  $\text{Cu}_{\text{Zn}}$  acceptor levels were located 0.72 eV above the valence band and the temperature dependence of dark conductivity indicated  $3 \times 10^{17} \text{ cm}^{-3}$  acceptors and  $10^{17} \text{ cm}^{-3}$  donors. The compensating donors could be impurities such as the halides, which are not detectable in spectrographic analysis, or they could be intrinsic

TABLE I. Variation of luminescence maxima with excitation intensity at 16°K.

Excitation intensity (photons $\text{cm}^{-2} \text{sec}^{-1}$ )	Energy of band maximum, eV	
	Red	Green
$6.3 \times 10^{14}$	1.953	2.340
$5.1 \times 10^{16}$	1.955	2.340
$3.0 \times 10^{17}$	1.963	2.340

<sup>14</sup> G. B. Stringfellow and R. H. Bube, *II-VI Semiconducting Compounds*, D. G. Thomas, Ed. (W. A. Benjamin, Inc., New York, 1967), p. 1315.

<sup>15</sup> G. B. Stringfellow and R. H. Bube, *Phys. Rev.* **171**, 903 (1968).

defects such as interstitial zinc. Red emission bands at 1.95 and 1.97 eV, to be discussed further in the present paper, and a green emission band at 2.34 eV are found, corresponding to transitions from free or weakly bound electrons to bound holes. Besides being the dominant acceptor centers, the  $\text{Cu}_{\text{Zn}}$  impurities are also sensitizing centers for *n*-type photoconductivity. All of the observed electrical, optical, and photoconductivity properties of ZnSe:Cu can be consistently described in terms of a multivalent copper impurity model involving self-compensation by the copper itself.

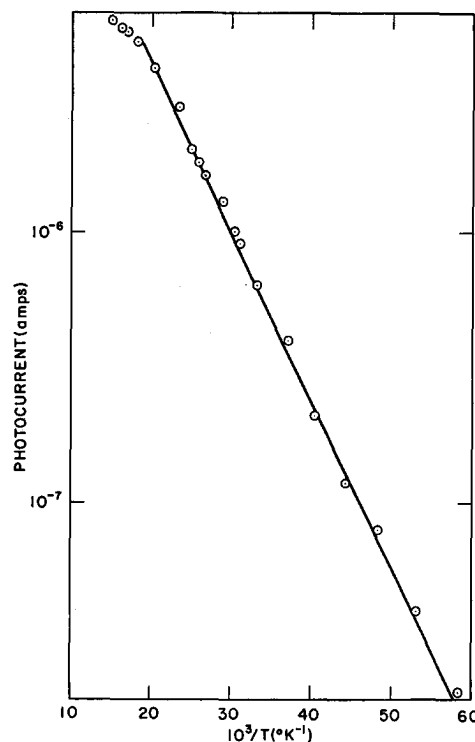


FIG. 2. Temperature dependence of the photocurrent between 10° and 60°K.

### Thermal Quenching of 1.95-eV Emission

At 16°K the emission spectrum of ZnSe:Cu shows a broad red band at 1.95 eV with a half-width of 0.18 eV. As the temperature is raised above 50°K, the luminescence intensity decreases as shown in Fig. 1. The intensity may be described by the expression  $I \propto T^{-3/2} \exp(0.012 \text{ eV}/kT)$ . The quenching of the 1.95-eV emission reveals a much less intense band at 1.97 eV, which quenches near 250°K with an activation energy of about 0.8 eV.

### Low-Temperature Intensity-Dependent Spectra

At 16°K, the position of the 1.95 eV band maximum shifts to higher energies with increasing excitation intensity, as summarized in Table I. For a three-order-of-magnitude increase in excitation intensity, the band maximum shifts by 10 mV.

### Low-Temperature Reduction in Electron Lifetime

The electron lifetime decreases exponentially with decreasing temperature below 50°K with an activation energy of 0.012 eV between 70° and 15°K, as shown in Fig. 2. Below 15°K, the lifetime again becomes temperature independent, and above 70°K it is constant until it quenches at about 250°K simultaneously with the 1.97-eV red emission. Related low-temperature effects have recently been described by Blount *et al.*<sup>16</sup> in ZnS, by Crandall<sup>17</sup> in CdS, and in the effects described as cryoluminescence by Jaszczyn-Kopec *et al.*<sup>18</sup> in ZnS.

### Pair-Emission Model

It is known that the luminescence transitions in ZnSe:Cu correspond to recombinations between free or weakly bound electrons and holes captured at copper acceptor centers.<sup>15</sup> It is also known from the same study that the electron cross section for capture of a free electron by a hole at a  $Cu_{Zn}'$  center is small,  $3 \times 10^{-19}$  cm<sup>2</sup>, so that these impurities act as sensitizing centers for *n*-type photoconductivity. The above experimental observations may be described in terms of a model in which a pair transition from a level 0.012 eV below the conduction band to the empty  $Cu_{Zn}'$  level 0.72 eV above the valence band gives rise to the 1.95-eV red emission, and a transition between the conduction band and this same empty  $Cu_{Zn}'$  level gives rise to the 1.97-eV red emission.

In the temperature range of the thermal quenching of the 1.95-eV luminescence, the occupancy of the  $Cu_{Zn}'$  centers is not thermally controlled. The electron density is found experimentally to be constant or slightly increasing. Thus the thermal quenching is due neither to the loss of holes from the ground state of the center, nor to a decrease in the density of free electrons. The thermal quenching must be attributed to ionization of the shallow levels lying 0.012 eV below the conduction band. The recombination kinetics can be analyzed for a related model consisting of a pair recombination center, a shallow trap, and an additional generalized recombination path. The calculation is given in the Appendix. The model predicts that at very low temperatures,  $n/N_c$  is temperature independent, but as the temperature is raised,  $n/N_c$  begins to increase approximately exponentially with an activation energy of  $E_t$ , the ionization energy of the shallow level. As the temperature increases further,  $n/N_c$  eventually becomes temperature independent again, and at this point the luminescence due to pair recombination quenches with a temperature dependence given by  $I \propto T^{-3/2} \exp(E_t/kT)$ . Thus it is possible to understand the quenching of the 1.95-eV luminescence near 50°K,

<sup>16</sup> G. H. Blount, A. C. Sanderson, and R. H. Bube, *J. Appl. Phys.* **38**, 4409 (1967).

<sup>17</sup> R. Crandall, *J. Appl. Phys.* **38**, 5425 (1967).

<sup>18</sup> P. Jaszczyn-Kopec, H. Kallmann, and B. Kramer, *Phys. Rev.* **165**, 901 (1968).

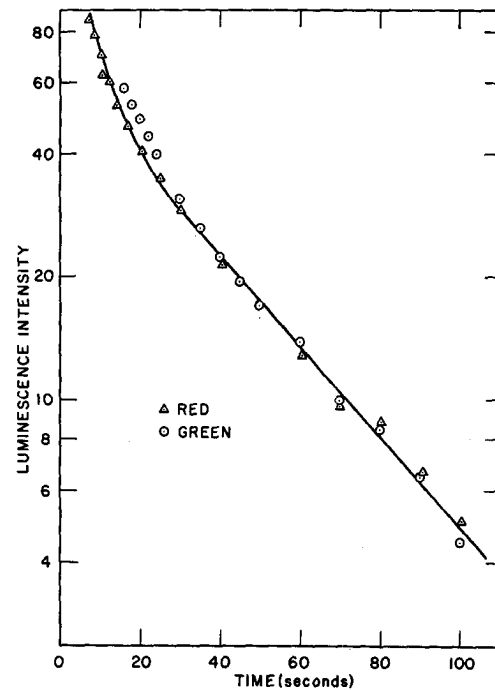


FIG. 3. Decay of red (1.95 eV) and green (2.34 eV) emission at 16°K.

and also the strong decrease in electron lifetime at lower temperatures, in terms of this model.

The suggestion that the red emission at 1.95 eV is due to a pair mechanism is also supported by the observation of a shift in this emission band with excitation intensity at low temperatures. At high excitation intensities, it is possible to saturate the pair-transition mechanism, i.e., to fill the upper state sufficiently that increasing the excitation intensity will not change its occupancy, while  $n$  still increases linearly with light intensity. Thus the ratio of the emission due to a transition from the conduction band directly to an empty  $Cu_{Zn}'$ , to the emission via the pair-transition route, is increased, and the emission band appears to shift to higher energies. This is similar to the phenomenon observed in GaP by Gershenson *et al.*<sup>13</sup>

### Long-Time Decay Measurements

Measurements of the decay of photoconductivity and luminescence were obtained either by directly recording on a Moseley *X-Y* recorder after shutter termination of excitation, or using a variable-speed chopper with display on a Tektronix 555 dual-beam oscilloscope. At 16°K, when the exciting radiation is removed, the red and green luminescence and the photoconductivity all drop sharply and then decay exponentially together with the same time constant of 30.6 sec., as shown in Fig. 3. The decay was investigated over the temperature range from 16° to 300°K. The results are plotted as log time constant vs  $1/T$  in Fig. 4. The time constant for the decay may be described by the expression

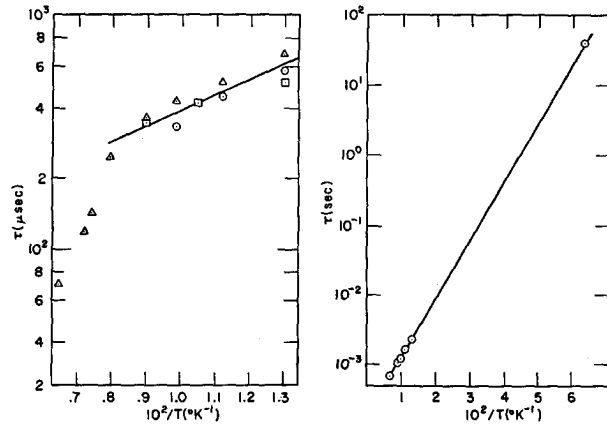


FIG. 4. Decay-time constant as a function of temperature for red emission  $\square$ , green emission  $\circ$ , and photoconductivity  $\Delta$ . Photoconductivity points deviating from the drawn straight line in the higher-temperature portion of the figure result from thermal quenching of photoconductivity.

$\tau = AT^{-3/2} \exp(0.012 \text{ eV}/kT)$ . If this decay is interpreted as being due to the emptying of shallow electron traps 0.012 eV below the conduction band, the data also permit the determination of the electron capture cross section for these traps of  $10^{-20} \text{ cm}^2$ .

It is proposed that this long-time decay is controlled by traps with a depth of 0.012 eV and a capture cross section for electrons of  $10^{-20} \text{ cm}^2$ . Such traps have more the characteristics of acceptorlike imperfections than of donors. The question must then be asked as to whether these same imperfections are also active in certain cases as the upper level in the observed pair transitions. It is conceivable that donor imperfections with an ionization energy of 0.012 eV are present and that these participate in the pair transitions, whereas acceptorlike 0.012 eV imperfections exhibit the trapping characteristics that are observed. A level at 0.012 eV below the conduction band, observed in Hall effect and conductivity measurements, has been reported by Aven and Segall<sup>19</sup> and Burmeister,<sup>20</sup> in high-conductivity ZnSe. Holton *et al.*<sup>21</sup> observed a trap 0.01 eV deep in low-temperature thermally stimulated conductivity and electron-spin resonance experiments. Since emission spectrographic analysis of the ZnSe:Cu crystals used shows no metallic donors present, it is likely that the shallow 0.012-eV levels, of whatever variety, are native defects.

The energetics of the luminescence emission form a possible basis for distinguishing between a donor and an acceptorlike characteristic for the upper level of the pair transition. In the simple picture of an unassociated donor-acceptor pair, the energy of the emission is given by

$$\Delta E = E_G - (E_D + E_A) + e^2/\epsilon r, \quad (1)$$

where  $E_G$  is the bandgap,  $E_D$  is the donor ionization energy,  $E_A$  is the acceptor ionization energy,  $\epsilon$  is the

<sup>19</sup> M. Aven and S. Begall, Phys. Phys. Rev. **130**, 81 (1963).

<sup>20</sup> R. A. Burmeister (private communication).

<sup>21</sup> W. C. Holton, M. deWit, and T. L. Estle (private communication).

dielectric constant, and  $r$  is the pair spacing. If the data of the present investigation are applied in Eq. (1), with  $E_G$  at least 2.70 eV,  $E_D = 0.01$  eV,  $E_A = 0.72$  eV, the observed value of  $\Delta E = 1.95$  eV yields a negative value of the Coulomb term ( $e^2/\epsilon r$ ). Admitting the difficulty of determining the value of  $\Delta E$  accurately for a broad band, the combination of this indicated Coulomb energy deficit with the small  $10^{-20} \text{ cm}^2$  measured electron cross section, is at least consistent with an identification of the 0.012-eV levels involved in pair transitions with the 0.012-eV levels involved in trapping. In this case, a kind of acceptor-acceptor pair would be indicated. Further low-temperature experiments to determine the charge on the shallow level are required to help resolve this question.

## APPENDIX

A model consisting of a shallow trap, a pair recombination center, and some other recombination center is used to investigate recombination kinetics as a function of temperature, as given in Fig. 5. Here  $\beta_i$  is the electron capture coefficient for the  $i$ th level,  $\alpha_i$  is the hole capture coefficient for the  $i$ th level,  $\gamma$  is the recombination probability within the pair center,  $P_i$  is the electron thermal escape probability from the  $i$ th level,  $N_i$  is the total density of the  $i$ th center, and  $n_i$  is the density of electron-occupied  $i$ th levels. The equations describing the equilibrium kinetics in the presence of an excitation rate  $f$  for electron-hole pairs are

$$f = n_1\gamma + n(N_3 - n_3)\beta_3 \quad (1)$$

$$n_4P_4 = n(N_4 - n_4)\beta_4 \quad (2)$$

$$n_1(P_1 + \gamma) = n(N_2 - n_2 - n_1)\beta_2 \quad (3)$$

$$n_1\gamma = pn_2\alpha_2 \quad (4)$$

$$n(N_3 - n_3)\beta_3 = pn_3\alpha_3 \quad (5)$$

$$p + (N_2 - n_2) + (N_3 - n_3) = n + n_4 + n_1. \quad (6)$$

Under the mathematically simplifying assumption that  $\beta_2 = \beta_3$ , Eqs. (1), (3), and (6) combine to give (neglecting  $p$  with respect to  $n$ )

$$f = n(n + n_4)\beta_2 - n_1P_1. \quad (7)$$

Two cases are suggested by Eq. (7): (a) the case of

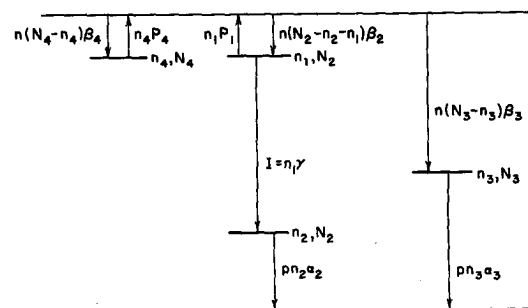


FIG. 5. Model used for the calculation of recombination kinetics for a system involving pair recombination, shallow traps, and other recombination processes.

low temperatures, where  $n_4 \gg n$ , and (b) the case of higher temperatures, where  $n_4 \ll n$ .

(a) Low-temperature case. Combining Eq. (7) with Eq. (2) gives

$$n^2 - n[(n_1 P_1 + f)/N_4 \beta_2] - [P_4(n_1 P_1 + f)/N_4 \beta_2 \beta_4] = 0, \quad (8)$$

with the solution

$$n = (n_1 P_1 + f)/2N_4 \beta_4 \pm \frac{1}{2} [(n_1 P_1 + f)^2/N_4^2 \beta_2^2 + 4P_4(n_1 P_1 + f)/N_4 \beta_2 \beta_4]^{1/2}. \quad (9)$$

The behavior of Eq. (9) depends on the relative magnitudes of  $n_1 P_1$  and  $f$ . At very low temperatures (e.g., below 15°K in our experimental case),  $n_1 P_1 \ll f$ , and  $n/N_c$  is essentially temperature independent. At slightly higher temperatures for which  $n_1 P_1 \gg f$ , the dominant

temperature-dependent term in both terms of Eq. (9) is  $\exp(-E_i/kT)$ , where  $E_i = E_1 = E_4$ , and hence  $n$  increases exponentially with increasing temperature.

(b) Higher-temperature case. In this temperature range,  $n_1$  is determined by thermal interchange with the conduction band, rather than by recombination, so that

$$n_1 \approx (n/N_c) N_2 \exp(E_i/kT). \quad (10)$$

Under these conditions, Eq. (1) becomes

$$f \approx n(N_3 - n_3) \beta_3. \quad (11)$$

$n$  is not temperature dependent in this range, and the luminescence intensity can be expressed as

$$I \propto n_1 \alpha T^{-3/2} \exp(E_i/kT). \quad (12)$$

In this range, therefore, the luminescence emission quenches with an activation energy of  $E_i$ .

## Time-Decay Characteristics for the Red Emission from GaP

F. E. HARPER, S. STRASSLER, AND B. W. HAKKI

*Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey*

(Received 29 January 1968)

The decay of the red emission from a Zn-O- and Te-doped GaP *p-n* junction was measured. The measurements were made for temperatures between 77°K and 298°K by using current pulses (0.5–2.0)  $\mu$ sec in duration and (10–200) A/cm<sup>2</sup> in amplitude. At low temperatures ( $T \leq 113^\circ\text{K}$  for the GaP studied here), the emission decayed like  $t^{-1}$  at long times, indicating that the emission was due to pair recombination (recombination of an electron and a hole bound to distant impurity levels). At high temperatures ( $T > 139^\circ\text{K}$ ), the emission decayed exponentially with a single time constant which was independent of the current amplitude and which decreased with increasing temperature. This result is consistent with the exciton decay mechanism recently found at low temperature by Morgan *et al.* and Henry *et al.* to account for a part of the red emission from GaP.

For some time the red emission from GaP doped with a deep donor, oxygen, and a shallow acceptor, zinc or cadmium, was believed to be largely due to pair recombination between electrons and holes bound, respectively, to distant donors and acceptors.<sup>1–4</sup> In the emitted spectrum several lines attributed to exciton decay were also present. Recently Morgan *et al.*<sup>5</sup> and Henry *et al.*<sup>6,7</sup> have made measurements of the photoluminescent red emission from GaP single crystals at low temperatures ( $T < 20^\circ\text{K}$ ) which cannot be interpreted as being due to the above pair recombination

mechanism. Instead, they show that the radiative mechanism involves both (a) the recombination of an electron, bound to a neutral complex, with a hole bound to a distant acceptor, or (b) the decay of an exciton bound to a deep Zn-O or Cd-O complex located approximately 0.4 eV below the conduction band. The oxygen level previously believed to be located 0.4 eV below the conduction band<sup>8</sup> is now thought to be much deeper as indicated by the infrared emission found at 1.4 eV and by the calculation of Dean *et al.*<sup>9</sup> which gives the ionization energy of the oxygen level as  $0.895 \pm 0.002$  eV.

We measured the decay of the red emission due to electroluminescence from a GaP *p-n* junction as a function of temperature for  $77^\circ\text{K} \leq T \leq 300^\circ\text{K}$  by using current pulses (0.5–2.0)  $\mu$ sec in duration and (5.0–100) mA or (10–200) A/cm<sup>2</sup> in amplitude. These measurements extended the temperature range previously reported, and furthermore they were made with a *p-n*

<sup>1</sup> J. J. Hopfield, D. G. Thomas, and M. Gershenson, Phys. Rev. Letters **10**, 162 (1963).

<sup>2</sup> D. G. Thomas, M. Gershenson, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

<sup>3</sup> F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, A1030 (1965).

<sup>4</sup> D. F. Nelson and K. F. Rodgers, Phys. Rev. **140**, A1667 (1965).

<sup>5</sup> T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968).

<sup>6</sup> C. H. Henry, P. J. Dean, D. G. Thomas, and J. J. Hopfield, International Conf. on Localized Excitations in Solids, Univ. of California, Irvine, Calif., Sept. 1967.

<sup>7</sup> C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).

<sup>8</sup> T. N. Morgan, Bull. Am. Phys. Soc. **11**, 188 (1966).

<sup>9</sup> P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. **168**, 812 (1968).