

## New Red Pair Luminescence from GaP†

C. H. HENRY AND P. J. DEAN

*Bell Telephone Laboratories, Murray Hill, New Jersey*

AND

J. D. CUTHBERT

*Bell Telephone Laboratories, Whippany, New Jersey*

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We report optical experiments showing that the low-temperature red luminescence in GaP doped with Cd (or Zn) acceptors arises in two ways: (a) from the recombination of electrons bound to neutral complexes involving Cd (or Zn) and O, with holes trapped at distant Cd (or Zn) acceptors producing pair spectra with novel properties; (b) from the decay of an exciton bound at these complexes, as recently reported by Morgan *et al.* Zeeman and isotopic shift experiments which provide information about the symmetry axis, electronic structure, and chemical identity of the exciton-impurity complex are also discussed. The concentrations of the neutral complexes in Zn- and Cd-doped GaP have been estimated from absorption measurements using oscillator strengths derived from the measured decay time of the exciton luminescence.

IN the past several years there has been an intensive effort to understand the origin of the red luminescence in GaP. Gershenson *et al.*<sup>1,2</sup> and Nelson<sup>3</sup> have attributed this luminescence to pair recombination involving the deep donor oxygen and the shallow acceptors Cd and Zn. In a recent paper, Morgan, Welber, and Bhargava<sup>4</sup> (MWB) reported a structured red luminescence in Cd- and O-doped GaP. This spectrum is characteristic of the recombination of an electron and hole trapped on a single site (bound exciton), rather than their recombination at donor-acceptor pairs distributed on different sites. They have attributed this decay to an exciton bound to Cd and O nearest neighbors. We have independently discovered this exciton luminescence and in this paper report (a) experiments determining the symmetry, level structure, lifetimes, and concentration of the exciton site, and verification that the center binding the exciton involves both Cd and O; (b) experiments showing that a second relatively featureless band, at slightly lower energies, exhibits a decay characteristic of recombination at electron trap-acceptor pairs of variable separations. We present strong evidence that this pair luminescence results from the recombination between holes at isolated Cd (or Zn) acceptors and electrons at the complex described above which behaves as a deep neutral electron trap. Unlike previously reported pair transitions,<sup>5</sup> the pair spectrum does not contain a Coulomb shift [see Eq. (1), below].

The exciton luminescence at 20°K [Fig. 1(a), curve I] shows a zero-phonon line A, followed by phonon replicas. The A transition is frozen out on cooling from 20 to 1.6°K, and a new transition B appears. Transition B is forbidden and can only be observed if strain or magnetic field are present, as shown in Figs. 2(a) and 2(b). Lines A and B both split anisotropically in a magnetic field. The splittings of the B line are shown in Fig. 2(d). The data were fitted by the solid theoretical curve assuming the site binding the exciton has a  $\langle 111 \rangle$  symmetry axis, that the excited states can be split into two levels, that the ground state is a singlet, and that the levels only split when a component  $H$  is parallel to the symmetry axis [see Fig. 2(c)]. The magnitude of the splitting was adjusted to fit the data for  $H$  along  $[100]$ . The magnetic splittings, the fact that the B transition is forbidden, and the dependence of the intensity of the B transition on  $H$  can be predicted on the basis of a simple model which assumes that the exciton is formed from an electron with  $J_z = \pm \frac{1}{2}\hbar$  and a hole with  $J_z = \pm \frac{3}{2}\hbar$ , where  $J_z$  is the angular momentum along the symmetry axis. From this analysis, we find  $g_e = 1.82 \pm 0.20$  and  $g_h = 0.98 \pm 0.05$ , in agreement with values obtained from Zeeman studies of much shallower bound exciton complexes in GaP.<sup>6</sup> These level assignments differ from those of MWB, which could not explain our data.<sup>7</sup>

The most striking features of the exciton spectrum are the narrow vibrational sidebands spaced by 7.0 meV. In crystals doped with Cd<sup>110</sup> and Cd<sup>114</sup> we have found an isotope shift for this vibrational energy of  $(1.36 \pm 0.20)\%$ , i.e.,  $\frac{3}{4}$  as large as the shift expected for Cd vibrating alone. We also observe a shift of the zero-

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<sup>1</sup> M. Gershenson, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, *J. Appl. Phys.* **36**, 1528 (1965).

<sup>2</sup> M. Gershenson, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, *J. Appl. Phys.* **37**, 483 (1966).

<sup>3</sup> D. F. Nelson and K. F. Rodgers, *Phys. Rev.* **140**, A1667 (1965).

<sup>4</sup> T. N. Morgan, B. Welber, and R. N. Bhargava, preceding paper, *Phys. Rev.* **166**, 751 (1968), hereafter referred to as MWB.

<sup>5</sup> See, e.g., J. J. Hopfield, D. G. Thomas, and M. Gershenson, *Phys. Rev. Letters* **10**, 162 (1963); F. M. Ryan and R. C. Miller, *Phys. Rev.* **148**, 858 (1966).

<sup>6</sup> D. G. Thomas, M. Gershenson, and J. J. Hopfield, *Phys. Rev.* **131**, 2397 (1963).

<sup>7</sup> MWB assign level A to be a triplet and level B to be a quartet. We find experimentally that these levels are each doublets. For  $H=0$ , MWB's assignments predict five nondegenerate transitions. We find only two transitions (A and B), each of which are 0.2-meV wide at 4°K. The no-phonon lines observed by MWB were 0.75 meV broad, because of instrumental broadening.

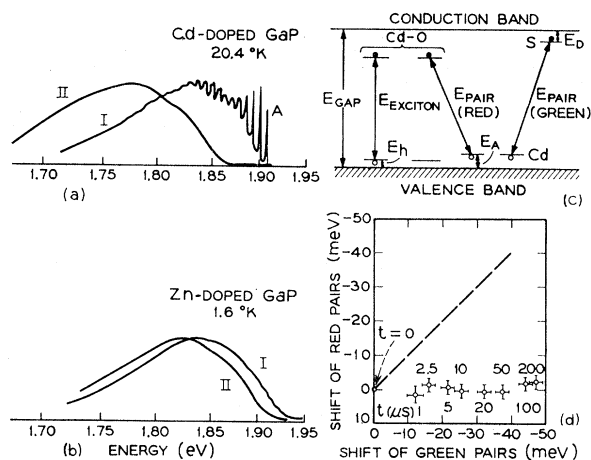


FIG. 1. (a) Curve I (Cd-O) exciton luminescence, curve II (Cd-O)-Cd pair luminescence. These bands were of comparable intensity; (b) curve I (Zn-O) exciton luminescence, curve II (Zn-O)-Zn pair luminescence; (c) level diagram showing the exciton and pair decays for Cd-doped GaP; (d) shift of the (Cd-O)-Cd pair luminescence versus the shift in the Cd-S pair luminescence with time after pulse excitation. The shifts were measured at the high-energy side half-maximum of each band. If the electron trap giving rise to the red pair luminescence was an ordinary ionized donor such as  $O^-$ , both the red and green pair bands would have shifted by comparable amounts as indicated by the dashed line.

phonon line A of 0.65 meV to higher energy in samples containing  $O^{18}$ . This result agrees with the oxygen-isotope experiment performed originally by MWB.<sup>8</sup> No shifts were observed in the other phonon replicas. This is not consistent with phonon assignments of MWB, who take the 48-meV mode to be a vibration involving the O atom.

The exciton decays exponentially with a decay time of 90 nsec from level A and 560 nsec from level B. From these lifetime measurements and from the measurement of the exciton absorption spectrum<sup>9</sup> (not shown), we find a maximum concentration of about  $2 \times 10^{16} \text{ cm}^{-3}$  for the complexes in Cd-doped crystals.

Spectrum II in Fig. 1(a)<sup>8</sup> is long lived and decays nonexponentially in a way that is characteristic of pair spectra.<sup>10</sup> We have followed its decay to 10 msec. The band has a shape and half-width that are very similar to the exciton spectrum if the phonon fine structure in the latter is smoothed out.

We are also able to distinguish exciton and pair bands in the Zn-doped crystals, as shown in Fig. 1(b). The luminescence was excited with 4880 Å light of an argon ion laser beam having a power of 40 mW. By focusing the laser beam, we were able to saturate the pair band

<sup>8</sup> We were motivated to repeat this experiment because the zero-phonon line reported by MWR was broad, making it difficult to check for O isotope-induced shifts in the phonon replicas. (See Ref. 7.)

<sup>9</sup> This spectrum was most easily observed in crystals cooled rapidly from 800°C after growth. Such crystals contain relatively high concentrations of free Cd acceptors.

<sup>10</sup> D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).

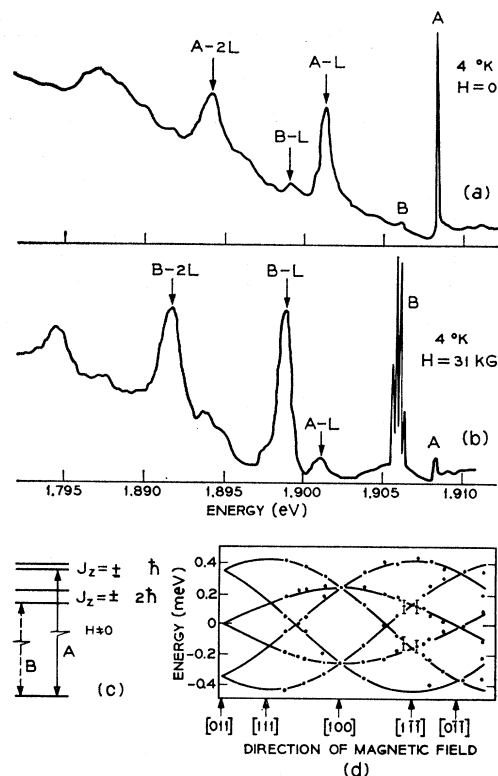


FIG. 2. (a) (Cd-O) exciton luminescence at 4°K with  $H=0$ ; (b) (Cd-O) exciton luminescence at 4°K with  $H=31 \text{ kg}$ . The six components result from the center having different orientations with respect to  $H$ . Transition B is forbidden for  $H=0$  and has an intensity proportional to the square of the component of  $H$  perpendicular to the [111] symmetry axis of the Cd-O complex; (c) level diagram; (d) splittings of transition B versus direction of  $H$  as  $H$  was rotated in a plane perpendicular to the [011] direction.

and observe the exciton band. The exciton spectrum has weak vibrational sidebands on the high-energy side, with a spacing of 6.0 meV. The zero-phonon line is not observable, presumably because of large phonon coupling. The exciton and pair bands are even more clearly distinguishable in time-resolved spectra and are then separated by  $25 \pm 2 \text{ meV}$ . Optimally, Zn- and O-doped crystals<sup>11</sup> contain up to  $5 \times 10^{16} \text{ cm}^{-3}$  of the Zn-O complexes.

The relative positions of the pair bands and exciton bands, shown in Figs. 1(a) and 1(b), can be explained by the level diagram in Fig. 1(c). If the Cd-O complex only traps an electron, pair decay can occur in which this electron recombines with a hole on a distant Cd acceptor. The exciton band and the pair band should have roughly the same shape (as observed), because the phonon coupling will be determined primarily by the deeply trapped electron. The energy separation between the pair band and the exciton band is  $E_A - E_h$  [see Fig. 1(c)]. We measure this separation to be

<sup>11</sup> Optimum doping condition for the red luminescence in Zn-doped GaP are discussed in Ref. 1.

$60 \pm 6$  meV for Cd-doped crystals and  $25 \pm 2$  meV for Zn-doped crystals. The acceptor binding energies are known to be  $E_A(\text{Cd}) = 95 \pm 2$  meV and  $E_A(\text{Zn}) = 62 \pm 2$  meV.<sup>12</sup> Thus for the Cd-O exciton  $E_h = 35 \pm 8$  meV and for the Zn-O exciton  $E_h = 37 \pm 4$  meV. We expect the hole to be bound to the trapped electron by an effective-mass binding energy, reduced by about 5 meV because the hole is not bound to a point charge and in addition by 5–10 meV because of the repulsion produced by the same short-range (non-Coulomb) potential that attracts the electron. If we take the effective-mass energy to be the same as the binding energy of the weakly bound Si acceptor,  $E_A(\text{Si}) = 46$  meV,<sup>12,13</sup> we would predict  $E_h \approx 31$ –36 meV, close to our experimental values.

The Zn pair band is more than  $48 \pm 4$  meV higher in energy than the Cd pair band (at 20°K).<sup>14</sup> If the electron were trapped on the same site in both cases, we would expect the pair bands to be separated by  $E_A(\text{Cd}) - E_A(\text{Zn}) = 33$  meV. We must conclude that the binding energy of the electron giving rise to the pair spectra changes in going from Zn-doped crystals to Cd-doped crystals. This result is consistent with the model and weighs against the idea that the electron is trapped on the neutral donor oxygen,<sup>1,2,3,15</sup> or at *any* electron trap which is independent of the nature of the acceptor.

We have heated Cd-doped crystals at 1000°C for several minutes and then cooled them rapidly to room temperature. This treatment caused a reduction of 3–10 in both the exciton and red pair luminescence relative to the green pair luminescence. This is further

<sup>12</sup> P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **18**, 122 (1967).

<sup>13</sup> Evidence will be presented in a forthcoming paper that the shallow acceptor attributed to Si in Ref. 12 is in fact due to C.

<sup>14</sup> Since the phonon interaction is stronger in the Zn pair band, the observed separation of  $48 \pm 4$  meV between the pair bands tends to *underestimate* the difference in  $E_A + E_T$  between the two spectra and therefore underestimates the discrepancy with the model in which the ionization energy  $E_T$  of the electron trap is invariant.

<sup>15</sup> Remote pair transitions involving isolated deep O donors have recently been discovered in the near infrared ( $\sim 1.5$  eV); P. J. Dean, C. H. Henry, and C. J. Frosch (unpublished).

evidence that the pair and exciton luminescence involve a common site which dissociates upon heating the sample to 1000°C.

In ordinary donor-acceptor pair recombination, the decay energy  $h\nu$  is given (aside from phonon cooperation) by

$$h\nu = E_{\text{gap}} - E_A - E_D + e^2/\epsilon r \quad (1)$$

for pairs of sufficiently large separation  $r$ .<sup>14,16</sup> This dependence on  $r$  causes the more closely spaced pairs, which decay first, to have higher energy. As a result, after pulse excitation, the high-energy side of the pair spectrum shifts with time to lower energies. In our case, the electron is trapped at a neutral complex and the equation for the decay energy does not contain the Coulomb term. This is conclusively verified by the data in Fig. 1(d). No shift with time was observed for the red pair band within the experimental error of  $\pm 3$  meV, while the green (Cd-S) pair band shifted by 47 meV under identical experimental conditions. A similar result was observed in Zn-doped crystals.

The deep electron trap has been shown to involve both Cd (or Zn) and O, has  $\langle 111 \rangle$  symmetry, and is neutral with no unpaired spin. A possible model is a nearest-neighbor Cd (or Zn)-O substitutional pair, as proposed by MWB. The exciton transitions are equivalent to the recombinations at nearest-neighbor O-Cd (or Zn) donor-acceptor pairs. The model proposed by MWB has been further strengthened by the recent observation of discrete transitions, accurately described by Eq. (1), at remote pairs of these donors and acceptors.<sup>15</sup>

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<sup>16</sup> D. G. Thomas, M. Gershenson, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).