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Free-to-Bound and Bound Exciton Transitions at Isoelectronic Impurities: GaP(Zn,O)

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We show, for sufficiently high temperatures and sufficiently weak majority-carrier binding energies, that the dominant radiative transition at an isoelectronic acceptor (donor) in p-type (n-type) material consists of the recombination of singly trapped minority carriers (bound by central-cell forces) with free majority carriers attracted by a Coulomb interaction. There are two reasons why the radiative recombination rate of the free-to-bound process is greater than the bound exciton process, which dominates at lower temperatures: (i) The population of free majority-carrier states greatly exceeds that of exciton states at higher temperatures, and (ii) the oscillator strength of the free-to-bound transition is greatly enhanced by the Coulomb attraction between the free carrier and the charged isoelectronic impurity. This enhancement is important for isoelectronic centers and is easily calculable from existing exciton models. We show that the free carrier attracted by a Coulomb interaction can be viewed as a continuum excited state of the bound exciton. When we apply the results of our calculations to the GaP(Zn, O) system, we find that the major part of the room-temperature luminescence from nearest-neighbor isoelectronic Zn-O complexes results from free-to-bound recombination and not exciton recombination as has been thought previously. Recent experiments on impulse excitation of luminescence in GaP(Zn, O) are reevaluated in the light of our calculations and are shown to be consistent with a strong free-to-bound transition. For deep isoelectronic centers with weakly bound majority carriers, we predict an overwhelming dominance of the free-to-bound process at 300 °K.

I. INTRODUCTION

Isoelectronic impurities have three distinct and coupled occupation or charge states, i.e., empty (neutral), singly occupied (charged), and exciton occupied (neutral). The three-state nature of isoelectronic impurities greatly complicates the recombination processes occurring at these impurities, as discussed in detail elsewhere.[1-3] It has been amply demonstrated[4] over the past several years that isoelectronic impurities are important radiative recombination centers in many wide-band-gap semiconductors. At low temperatures, where free carriers are absent, the luminescence from isoelectronic centers is due principally to excitonic recombination. However, at high temperatures, where thermally generated free-carrier concentrations are large and where thermal dissociation of excitons occurs, we find that excitonic recombination becomes less probable, while at the same time free-to-bound recombination originating from the singly charged state becomes increasingly more probable. As a result, we anticipate that the high-temperature emission from isoelectronic centers will in general be made up of a combination of excitonic and free-to-bound emissions. These two processes are manifestations of the same basic interaction. That is, the excitonic process involves radiative recombination of Coulomb-attracted bound electron-hole pairs, whereas the free-to-bound process involves radiative recombination of trapped minority carriers with Coulomb-attracted free majority carriers. This rather special situation is of particular importance for three-state isoelectronic impurities where the singly charged state can be regarded as the excited continuum state of the neutral ground exciton state.

The purpose of this paper is to calculate both the excitonic and free-to-bound lifetimes for isoelectronic centers taking into account electron-hole correlations arising from the basic Coulomb interaction. In our calculation we do not consider coupling with the lattice. We show that the ratio of free-to-bound to excitonic lifetimes depends only on the exciton binding energy and the free-particle density. Thus, it is always possible, in principle, to determine the relative importance of free-to-bound and excitonic processes. Our results make use of Faulkner's calculations[5] for bound exciton transitions at the nitrogen isoelectronic center in GaP, and Elliot's work[6] on the theory of optical absorption in the vicinity of the band edge of semiconductors. The calculation of free-to-bound and excitonic lifetimes closely parallels the calculation of the absorption intensities of exciton and interband transitions in semiconductors. (In principle, these lifetimes can be obtained from the impurity absorption coefficient using detailed balance,[7] although phonon cooperation makes this difficult in practice, particularly for deep impurities such as the Zn-O complex in GaP.)

We apply the results of our calculations to the GaP(Zn, O) system and show that the major part of the room-temperature luminescence from nearest-neighbor isoelectronic Zn-O complexes results from free-to-bound recombination and not exciton recombination as has been thought previously.[1-3,8,9] Because the free-to-bound and excitonic transitions are so similar in GaP(Zn, O), they overlap both spectrally and temporally and are thus difficult to separate. Recently, impulse-excited luminescence experiments have been conducted using GaP(Zn, O) electroluminescent diodes.[10] In impulse experiments,[10-12] the rate of buildup of the luminescence is controlled by the free-to-bound process.[12] By fitting theoretical expressions for the impulse-excited luminescence which include the free-to-bound process, we estimate the room-temperature free-to-bound lifetime from Zn-O centers as about 1 μsec for a Zn concentration of 10^{18} cm^{-3}. This value is in reasonable agreement with our theoretical estimate of 0.8 μsec.

II. THEORY OF EXCITON AND FREE-TO-BOUND LIFETIMES

A schematic diagram of the three-state model[1-3] for an isoelectronic center in p-type material is shown in Fig. 1. Figure 1(a) indicates how the unoccupied center (concentration N_t^0) is converted into an electron-occupied center (concentration N_t^-) by capture of minority carriers (lifetime τ_{nt}). Figure 1(b) indicates how the electron-occupied center reverts back to the unoccupied state through electron thermalization (τ_{tn}), nonradiative Auger recombination (τ_{en}),[2,13] or radiative (free-to-bound) recombination (τ_{er}). If majority-carrier holes are captured (τ_{pt}) through Coulomb attraction by the singly charged electron-occupied centers, bound excitons form (concentration N_t^x). The excitonic configuration, shown in Fig. 1(c), will transform into either the electron-occupied or -unoccupied configurations by hole thermalization (τ_{tp}), radiative (excitonic) recombination (τ_{xr}), or nonradiative Auger recombination (τ_{xn}),[2,13] respectively. Owing to the multiplicity of lifetime parameters, the description of recombination at isoelectronic centers is generally complex.[1-3] Moreover, the identification of radiative processes is difficult, especially in the high-temperature limit where nonradiative Auger processes are present and where phonon interactions (lattice relaxation) broaden lines appreciably. We now show that the basic radiative lifetime parameters τ_{xr} and τ_{er} can be computed in the absence of phonon interactions.

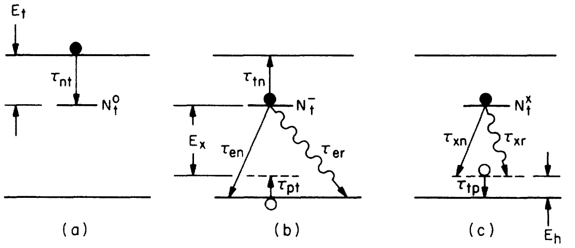

FIG. 1. Schematic representation of electron and hole recombination at an isoelectronic center. (a) Conversion of N_t^0 state into N_t^- state by electron capture (τ_{nt}). (b) Conversion of N_t^- state into N_t^0 state by thermalization (τ_{tn}), and by radiative (τ_{er}) and nonradiative Auger (τ_{en}) recombination. Also indicated is conversion of N_t^- state into N_t^x state by hole capture (τ_{pt}). (c) Conversion of N_t^x state into N_t^0 state by radiative (τ_{xr}) and nonradiative Auger (τ_{xn}) recombination. Also shown is conversion of N_t^x state into N_t^- state by hole emission (τ_{tp}). Energy levels E_t and E_h refer, respectively, to the electron and hole binding energies of the isoelectronic center.

Several calculations[14-16] exist in the literature for the strengths of optical transitions at bound-exciton impurity complexes. We follow here the derivation given by Faulkner,[5] who considered explicitly the absorption due to the nitrogen isoelectronic center in GaP. The momentum matrix element for optical transitions is of the form[5]

$$\vec{p}_{ti} = \int d^3k_e \int d^3k_h \, F(\vec{k}_e, \vec{k}_h) \, \langle c\vec{k}_e | \vec{p} | v\vec{k}_h \rangle \, . \qquad (1)$$

In this equation $\langle c\vec{k}_e | \vec{p} | v\vec{k}_h \rangle$ is the momentum matrix element between conduction- and valence-band Bloch states, the k integrations are limited to the Brillouin-zone volume, and the expansion coefficient $F(\vec{k}_e, \vec{k}_h)$ is the exciton envelope function in the momentum representation, satisfying the Schrödinger equation[5]

$$[E - E_c(\vec{k}_e) + E_v(\vec{k}_h)]\, F(\vec{k}_e, \vec{k}_h)$$

$$= \int d^3q\, [\langle c\vec{k}_e | \mathcal{V} | c\vec{q}\rangle\, F(\vec{q}, \vec{k}_h) - \langle v\vec{q} | \mathcal{V} | v\vec{k}_h\rangle\, F(\vec{k}_e, \vec{q})]$$

$$- (4\pi e^2/\epsilon)\, (2\pi)^{-3} \int d^3q\, q^{-2}\, F(\vec{k}_e + \vec{q}, \vec{k}_h + \vec{q}). \quad (2)$$

Here, $E_c(\vec{k}_e)$ and $E_v(\vec{k}_h)$ are the conduction- and valence-band energies, respectively, and the matrix elements involving the potential $\mathcal{V}(\vec{r})$ of the isoelectronic impurity are between Bloch states in the same band. (Only a single conduction and valence band are assumed for simplicity.) To a good approximation, the wave vector of the emitted photon is zero, which then requires $\vec{k}_e = \vec{k}_h$ from momentum conservation. Thus $\vec{p}_{fi}$ simplifies to

$$\vec{p}_{fi} = (8\pi^3/V) \int d^3k\, F(\vec{k}, \vec{k})\, \langle c\vec{k} | \vec{p} | v\vec{k}\rangle, \quad (3)$$

where V is the crystal volume and $\langle c\vec{k} | \vec{p} | v\vec{k}\rangle$ is the interband momentum matrix element between the periodic parts of the Bloch functions at $\vec{k}$, i.e.,

$$\langle c\vec{k} | \vec{p} | v\vec{k}\rangle = (V/8\pi^3) \int_{\text{cell}} d^3r\, u^*_{c\vec{k}}(\vec{r}) \vec{p}\, u_{v\vec{k}}(\vec{r})$$

$$\equiv (V/8\pi^3) \vec{p}_{cv}(\vec{k}). \quad (4)$$

Suppose we write the exciton envelope function as a product function

$$F(\vec{k}_e, \vec{k}_h) = f_e(\vec{k}_e)\, f_h(\vec{k}_h). \quad (5)$$

We wish to calculate $\vec{p}_{fi}$ in two cases. In the first, the hole is bound to the center in a shallow s-like state, while in the second the hole is in a Coulomb-attracted continuum state. In either case the hole wave function $f_h(\vec{k})$ will be very strongly peaked about the valence-band maximum at $\vec{k} = 0$. Since $f_h(\vec{k})$ will be much more rapidly varying in this region than either $f_e(\vec{k})$ [see, for example, Eq. (3.19) of Ref. 5] or $\langle c\vec{k} | \vec{p} | v\vec{k}\rangle$, we may approximate Eq. (3) by the expression

$$\vec{p}_{fi} = f_e(0) \vec{p}_{cv}(0) \int d^3k\, f_h(\vec{k}). \quad (6)$$

By writing the momentum wave function f_h in terms of its Fourier transform φ_h in the spatial representation and converting from momentum matrix elements to electric dipole matrix elements $\vec{\mu}$ $[\vec{\mu}_{cv} = \int_{\text{cell}} d^3r\, u^*_{c0}(\vec{r}) \vec{r} u_{v0}(\vec{r})]$, we can rewrite Eq. (6) as

$$\vec{\mu}_{fi} = (E_\Gamma/E) \vec{\mu}_{cv} f_e(0)\, \varphi_h(\vec{r} = 0), \quad (7)$$

where E_Γ is the direct energy gap at $\vec{k} = 0$ and E is the transition energy. Equation (7) is in the same form as that of expressions derived elsewhere[14–16] for direct-gap materials. To evaluate the radiative lifetime τ_r, we make use of the standard formula[17] and obtain

$$\frac{1}{\tau_r} = \left(\frac{4e^2}{3\hbar^4 c^3}\right) E E_\Gamma^2\, |\mu_{cv}|^2 |f_e(0)|^2 |\varphi_h(0)|^2. \quad (8)$$

The excitonic lifetime τ_{xr} is governed by the wave function for the bound-hole states. For the lowest-lying s state, we have[6]

$$|\varphi_h(0)|^2 = (\pi a_h^3)^{-1},$$

where a_h is the effective Bohr radius of the hole (or exciton). The exciton lifetime is therefore given by

$$\frac{1}{\tau_{xr}} = \left(\frac{4e^2}{3\hbar^4 c^3}\right) |\mu_{cv}|^2 |f_e(0)|^2 E_x E_\Gamma^2 \left(\frac{1}{\pi a_h^3}\right), \quad (9)$$

where E_x is the exciton transition energy.

The free-to-bound lifetime τ_{er} associated with continuum hole states involves an integration over the thermal distribution of valence-band hole states, i.e.,

$$\frac{1}{\tau_{er}} = \int_0^\infty \left(\frac{4e^2}{3\hbar^4 c^3}\right) |\mu_{cv}|^2 |f_e(0)|^2 (E_x + E_h + E_v) E_\Gamma^2$$

$$\times |\varphi_{er}(0)|^2\, V f(E_v)\, \rho(E_v)\, dE_v, \quad (10)$$

where E_h is the hole binding energy, E_v is the kinetic energy of a hole in the valence band, $f(E_v)$ is the Fermi-Dirac distribution function, and $\rho(E_v)$ is the valence-band density-of-states function. The function $\varphi_{er}(0)$ in Eq. (10) is the Coulomb-excited-state wave function,[6] given by

$$|\varphi_{er}(0)|^2 = \pi\alpha e^{\pi\alpha}/V \sinh\pi\alpha, \quad (11)$$

where

$$\alpha = (E_h/E_v)^{1/2}. \quad (12)$$

The factor $f(E_v)\, \rho(E_v)$ in the integrand of Eq. (10) undergoes a maximum near $E_v \sim kT$ and decreases exponentially for $E_v > kT$. Over the energy range where $f(E_v)\, \rho(E_v)$ is appreciable (i.e., $0 < E_v <$ several kT), α is large, with the result that

$$|\varphi_{er}(0)|^2 \approx 2\pi\alpha/V. \quad (13)$$

By inserting this value into Eq. (10) and replacing $E_x + E_h + E_v$ by $E_x + E_h$, we obtain

$$\frac{1}{\tau_{er}} = \left(\frac{8\pi e^2}{3\hbar^4 c^3}\right) |\mu_{cv}|^2 |f_e(0)|^2 (E_x + E_h) E_\Gamma^2 E_h^{1/2}$$

$$\times \int_0^\infty \frac{f(E_v)\, \rho(E_v)\, dE_v}{E_v^{1/2}}. \quad (14)$$

In the nondegenerate limit, it is easy to show, assuming spherical bands, that Eq. (14) reduces to

$$\frac{1}{\tau_{er}} = \left(\frac{16\sqrt{\pi}\, e^2}{3\hbar^4 c^3}\right) |\mu_{cv}|^2 |f_e(0)|^2 (E_x + E_h) E_\Gamma^2 \left(\frac{E_h}{kT}\right)^{1/2} p, \quad (15)$$

where p is the free-hole density.

The ratio of the excitonic to free-to-bound lifetime is independent of the interband matrix element and the envelope function $f_e(0)$ and is given by

$$\frac{\tau_{xr}}{\tau_{er}} = 4\pi^{3/2} a_h^3 \left(\frac{E_h}{kT}\right)^{1/2} \left(\frac{E_x + E_h}{E_x}\right) p. \tag{16}$$

Although this equation was derived in the limit where coupling to the lattice is absent, we might reasonably expect that both τ_{xr} and τ_{er} will be affected by phonon interactions in the same way, and that, as a consequence, Eq. (16) should also apply in the presence of lattice relaxation. Support for this contention is provided by the experimental observation that the dominant coupling between the bound exciton and the lattice is via the particle bound by central-cell forces. Thus, for the Zn-O, Cd-O,[8,9] and Bi[18] centers in GaP luminescence from the N_t^- and N_t^x states have shown very similar phonon structure.

III. LIFETIME PARAMETERS FOR THE Zn-O COMPLEX IN GaP

The radiative lifetimes for the Zn-O complex in GaP are now easily calculated. For a net Zn acceptor concentration $N_A = 10^{18}$ cm^{-3}, we have at room temperature $p = 6.76 \times 10^{17}$ cm^{-3} and $E_h = 26$ meV.[2,13] The exciton transition energy is $E_x \approx 1.8$ eV.[8,9] The effective Bohr radius of the bound hole is estimated from the relation

$$E_h a_h = e^2/2\epsilon \approx 0.65 \text{ eV Å} \tag{17}$$

to be $a_h \approx 25$ Å. Substituting these values into Eq. (16) gives

$$\tau_{xr}/\tau_{er} \approx 0.25. \tag{18}$$

The exciton lifetime was measured at low temperature[9] to be $\tau_{xr} = 100$ nsec. It is thought that as a result of screening by free holes[2] the room-temperature lifetime for $N_A = 10^{18}$ cm^{-3} should be $\tau_{xr} = 200$ nsec. Using this value, we estimate from Eq. (18) a free-to-bound lifetime of

$$\tau_{er} \approx 800 \text{ nsec} \tag{19}$$

or

$$\tau_{er} \approx \frac{540 \times 10^{18}}{p} \text{ nsec}. \tag{20}$$

It should be noted that the Coulomb contribution to τ_{er} is quite large. For example, if $|\varphi_{er}(0)|^2$ were equal to $1/V$ in Eq. (10), we would find in place of Eq. (15) the result

$$\frac{1}{\tau_{er}^0} = \left(\frac{4e^2}{3\hbar^4 c^3}\right) |\mu_{cv}|^2 |f_e(0)|^2 (E_x + E_h) E_\Gamma^2 p. \tag{21}$$

Thus the ratio τ_{er}^0/τ_{er} is given by

$$\tau_{er}^0/\tau_{er} = 4\sqrt{\pi}\,(E_h/kT)^{1/2}. \tag{22}$$

In the case of the Zn-O complex in GaP, we find

$$\tau_{er}^0/\tau_{er} \approx 7, \tag{23}$$

which leads us to conclude that an upper bound for the free-to-bound lifetime is

$$\tau_{er}^0 \approx 5600 \text{ nsec}. \tag{24}$$

The model which leads to this upper bound is oversimplified and is believed to be unphysical. The model which leads to the lower bound $\tau_{er} = 800$ nsec includes the important interactions and is believed to provide a realistic estimate for the free-to-bound lifetime.

In previous papers[1-3] an exciton occupancy factor f was defined by the relations

$$\begin{aligned} N_t^x &= f N_t^e, \\ N_t^- &= (1-f) N_t^e, \end{aligned} \tag{25}$$

where $N_t^e = N_t^x + N_t^-$ is the total electron-occupied concentration of isoelectronic centers. Explicit expressions for f were given in terms of the various lifetime parameters in Fig. 1 and the hole concentration. In terms of the f factor, the ratio of free-to-bound to exciton luminescence is given by

$$L_{er}/L_{xr} = [(1-f)/f]\,(\tau_{xr}/\tau_{er}), \tag{26}$$

where τ_{xr}/τ_{er} is given by Eq. (16). Using Eq. (26) we can estimate the relative importance of free-to-bound and excitonic transitions at any temperature and at any hole concentration. For the case of Zn-O in GaP it has been shown[2] that for $N_A = 10^{18}$ cm^{-3} the occupancy factor f including screening effects[2,13] is close to 0.1. If screening effects are neglected, then f assumes its thermal equilibrium value close to 0.2. Substituting these values for f and $\tau_{xr}/\tau_{er} = 0.25$ into Eq. (26) gives upper and lower bounds on L_{er}/L_{xr}, i.e.,

$$1.0 \le L_{er}/L_{xr} \le 2.3, \tag{27}$$

implying that a major fraction of the total room-temperature luminescence from GaP(Zn, O) is due to free-to-bound transitions. If τ_{er} were as long as 5600 nsec, the ratio would be $L_{er}/L_{xr} \approx 0.3$, implying that, at the very least, the free-to-bound luminescence is an appreciable fraction of the total luminescence.

Although the Zn-O isoelectronic complex has been our primary interest in this discussion, the results can be applied generally to yield a lower bound to the ratio L_{er}/L_{xr} for any isoelectronic impurity as a function of the binding energy E_h of the Coulomb-attracted carrier. From the definition[2] of f, one can easily show that

$$(1-f)/f > (N_v/p\beta) e^{-E_h/kT},$$

where N_v is the effective density of states associated with the Coulomb-attracted carrier, and β is its degeneracy factor. Using this inequality and replacing $E_x + E_h$ in Eq. (16) by E_x, we find from Eqs. (16), (17), and (26) a *lower bound* for L_{er}/L_{xr}:

$$\left(\frac{L_{er}}{L_{xr}}\right)_{\min} = \frac{4\pi^{3/2} N_v e^{-E_h/kT}}{\beta (kT)^{1/2} E_h^{5/2}} \left(\frac{e^2}{2\epsilon}\right)^3 . \tag{28}$$

In Fig. 2 we plot $(L_{er}/L_{xr})_{\min}$ vs E_h at 77 and 300 °K using constants appropriate to GaP in Eq. (28). From these results we expect that the free-to-bound process dominates the excitonic process for $E_h < 30$ meV at room temperature. For very shallow bound particles, Fig. 2 predicts the free-to-bound process to be of overwhelming importance at room temperature.

It should be pointed out that the steps leading to Eq. (28) have tacitly assumed that the effective charge Ze binding the hole at the charged isoelectronic impurity is of unit value ($Z = 1$). For GaP : N, where the electron wave function is expected to be spread out over the unit cell, one might well anticipate that $Z < 1$ since the 1*s* wave function assumed for the hole is nonvanishing at the origin. Such a view seems to be supported by the observation that the binding energy of the hole,[5] $E_h \approx 10$ meV, is much less than the effective-mass binding energy E_A of acceptors in GaP, i.e., $E_A \approx 50$ meV.[19] One may attribute such a reduction either to a reduced effective charge Z or a reduced effective mass m_h^* for the bound hole, through the relation

$$E_h = Z^2 e^4 m_h^* / 2\epsilon^2 \hbar^2 . \tag{29}$$

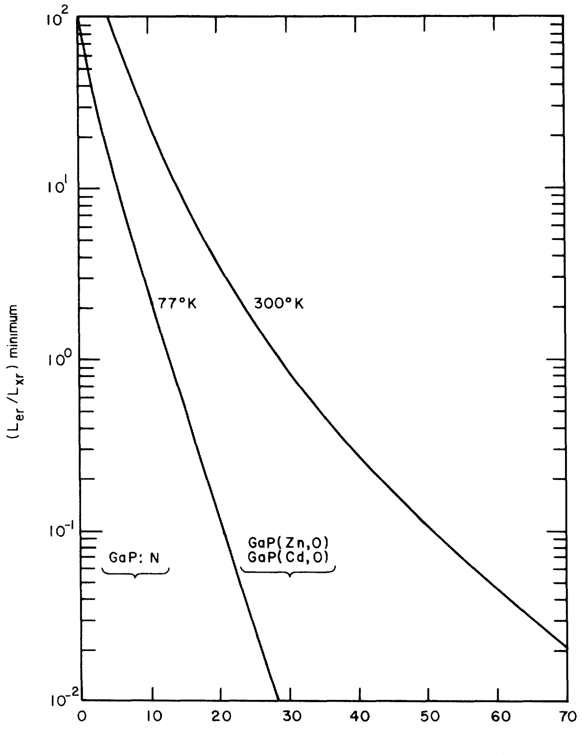

FIG. 2. Lower bound of the ratio L_{er}/L_{xr} vs the majority-carrier binding energy E_h using the following constants in Eq. (28) appropriate to Zn-O in GaP: $\beta = 2$, $\epsilon = 10.75$, $N_v = 3.98 \times 10^{15} T^{3/2}$ cm^{-3}. Two ranges of E_h are designated which are appropriate to important isoelectronic centers in GaP.

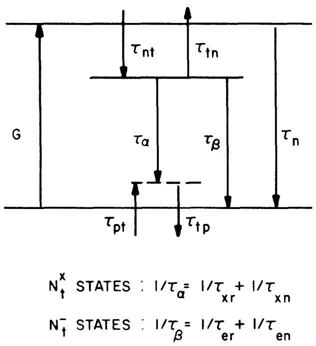

FIG. 3. Schematic diagram of two-path model for recombination of minority carriers in GaP(Zn, O). After generation by excitation G, minority carriers can be captured by Zn-O centers (τ_{nt}) or can be shunted to the valence band by unspecified residual impurities (τ_n). After capture, electrons may be thermalized (τ_{tn}) or may recombine with holes. Recombination with free holes from N_t^- states occurs in a lifetime τ_β. Alternatively, a hole is captured (τ_{pt}) to form bound excitons (N_t^x states) which recombine in a lifetime τ_α, or are decomposed by thermal emission of the trapped hole (τ_{tp}).

If one attributes the total reduction in the binding energy E_h to a reduced effective charge Z, one finds $Z = 0.45$. On the other hand, a variational calculation for Z performed by one of us (J. M. D.), and to be presented elsewhere, results in $Z = 0.91$. It is a straightforward matter to show that for $Z < 1$, the right-hand side of Eq. (28) is multiplied by a factor Z^4. Thus, for GaP : N, the results of Fig. 2 should be lowered by a factor ranging from 0.04 to 0.7 corresponding to $0.45 < Z < 0.91$. We are more inclined to the upper limits of these values, and suggest that a major factor in reducing E_h in Eq. (29) is a reduced effective mass, possibly resulting from the repulsive interaction between the hole and the central cell.

IV. IMPULSE-EXCITED LUMINESCENCE

Impulse-excited luminescence experiments have recently been conducted on GaP electroluminescent diodes.[10] An analysis of the impulse response,[10] assuming that the room-temperature luminescence was proportional to the instantaneous exciton population only, suggested that the initial rise of the luminescence depended on the hole capture time τ_{pt} in Fig. 1. We show that owing to the presence of the free-to-bound transition the rate of production of electron-occupied states, which depends on the minority-carrier lifetime, controls the buildup of the luminescence. By fitting our expressions for the impulse-excited luminescence[12] to the available experimental data,[10] we find that $\tau_{er} \approx 1$ μsec gives a good fit to the data. This value is in reasonable agreement with our theoretical estimates.

Referring to Figs. 1 and 3, the general nonlinear differential equations describing minority-carrier (n) recombination are

$$\dot{n} = G + (n_t/\tau_{nt})(N_t^-/N_t) - (n/\tau_{nt})(N_t^0/N_t) - n/\tau_n , \quad (30)$$

$$\dot{N}_t^- = (n/\tau_{nt})(N_t^0/N_t) + (p_h/\tau_{pt})(N_t^x/N_t)$$
$$- (n_t/\tau_{nt})(N_t^-/N_t) - (p/\tau_{pt})(N_t^-/N_t) - N_t^-/\tau_\beta , \quad (31)$$

$$\dot{N}_t^x = (p/\tau_{pt})(N_t^-/N_t) - (p_h/\tau_{pt})(N_t^x/N_t) - N_t^x/\tau_\alpha , \quad (32)$$

$$N_t = N_t^0 + N_t^- + N_t^x ; \quad (33)$$

$$1/\tau_{tn} = (1/\tau_{nt})(n_t/N_t), \quad 1/\tau_{tp} = (1/\tau_{pt})(p_h/N_t), \quad (34)$$

where n_t and p_h are the Shockley-Read n_1 coefficients[20] for N_t^- and N_t^x, respectively, and τ_n represents a nonradiative shunt path for recombination of minority carriers through centers other than the isoelectronic centers (see Ref. 2). It can be shown[10,12] that the solutions to the linearized equations obtained when $N_t^0/N_t \approx 1$ take the following form when G is an impulse [initial conditions $N_t^x(0) = N_t^-(0) = n(0) = 0$]:

$$N_t^x(t) = N\left(\frac{p}{N_t}\right)\left(\frac{\tau_1\tau_2\tau_3}{\tau_{nt}\tau_{pt}}\right)\left(\frac{\tau_1 e^{-t/\tau_1}}{(\tau_1-\tau_2)(\tau_1-\tau_3)} + \frac{\tau_2 e^{-t/\tau_2}}{(\tau_2-\tau_1)(\tau_2-\tau_3)} + \frac{\tau_3 e^{-t/\tau_3}}{(\tau_3-\tau_1)(\tau_3-\tau_2)}\right) \quad (35)$$

and

$$N_t^-(t) = N\left(\frac{\tau_1\tau_2\tau_3}{\tau_{nt}}\right)\left(\frac{[(\tau_1/\tau_\alpha)+(\tau_1/\tau_{tp})-1]}{(\tau_1-\tau_2)(\tau_1-\tau_3)}\,e^{-t/\tau_1} + \frac{[(\tau_2/\tau_\alpha)+(\tau_2/\tau_{tp})-1]}{(\tau_2-\tau_1)(\tau_2-\tau_3)}\,e^{-t/\tau_2} + \frac{[(\tau_3/\tau_\alpha)+(\tau_3/\tau_{tp})-1)]}{(\tau_3-\tau_1)(\tau_3-\tau_2)}\,e^{-t/\tau_3}\right), \quad (36)$$

where N is the strength of the impulse. The lifetimes τ_1, τ_2, and τ_3 can be obtained straightforwardly using Laplace transform methods.[10,12] They represent three basic decay modes of the system shown in Figs. 1 and 3 (i.e., τ_α, τ_β, and τ_n) and contain implicitly the coupling parameters τ_{nt} and τ_{pt} which mix the N_t^x, N_t^-, and n states.

We now show the behavior of the impulse-excited luminescence $L(t)$ given by

$$L(t) = N_t^x(t)/\tau_{xr} + N_t^-(t)/\tau_{er} . \quad (37)$$

The lifetime parameters for GaP(Zn, O) used in our calculations are listed in Table I. These parameters were determined elsewhere.[1,2] Figure 4 gives curves of the luminescence from N_t^x states ($L_x = N_t^x/\tau_{xr}$) and N_t^- states ($L_- = N_t^-/\tau_{er}$), as well as the total luminescence $L = L_x + L_-$. The only unspecified lifetime parameter is the shunt-path lifetime τ_n (see Fig. 3). In Fig. 4(a) we show the expected behavior for $\tau_n = 40$ nsec, a typical value for GaP(Zn, O),[2] and in Fig. 4(b) we give curves for a very short lifetime $\tau_n = 1$ nsec corresponding to one of the electroluminescent modes of excitation reported elsewhere.[10] Note that L_- rises with an initial slope equal to the minority-carrier lifetime $\tau_m = \tau_n\tau_{nt}/(\tau_n + \tau_{nt})$ in each case. The L_x response is delayed by the effect of τ_{pt}. The curve for the total luminescence in Fig. 4(b) fits the published experimental data,[10] which are shown as open-circle points. We conclude from the fit that $\tau_{er} \approx 1$ μsec for a Zn acceptor concentration of $N_A \approx 10^{18}$ cm^{-3}.

We expect that as τ_n decreases, the luminescence output will decrease in amplitude but will rise more rapidly. These expectations are borne out in the curves shown in Fig. 5 where we give plots of total luminescence vs time for $\tau_n = 100$, 40, and 1 nsec. It should be clear from these curves that impulse excitation of the luminescence provides a means for

TABLE I. Lifetime parameters for GaP(Zn, O) corresponding to a zinc concentration of 10^{18} cm^{-3} and a Zn-O trap concentration of 10^{16} cm^{-3}. (To compute the concentration and temperature dependence of τ_{pt} and τ_{xr} see Ref. 2. τ_{er} is temperature dependent through the hole concentration p. For $N_A = 10^{18}$ cm^{-3}, $p = 6.76 \times 10^{17}$ cm^{-3}.)

Electron and hole capture cross sections

$\sigma_{nt} = 2 \times 10^{-16}$ cm^2

$\sigma_{pt} = \dfrac{3.6}{T} \times 10^{-16}$ cm^2

Lifetimes at 300 °K

$\tau_{nt} = (v\sigma_{nt}N_t)^{-1} = 17.8$ nsec

$\tau_{tn} = (N_t/n_t)\tau_{nt} = 167$ nsec

$\tau_{pt} = (v\sigma_{pt}N_t)^{-1} = 7.9$ μsec

$\tau_{tp} = (N_t/p_h)\tau_{pt} = 20$ nsec

$\tau_{xr} = 200$ nsec (includes screening)

$\tau_{er} = \dfrac{6.76}{p} \times 10^{17}$ μsec

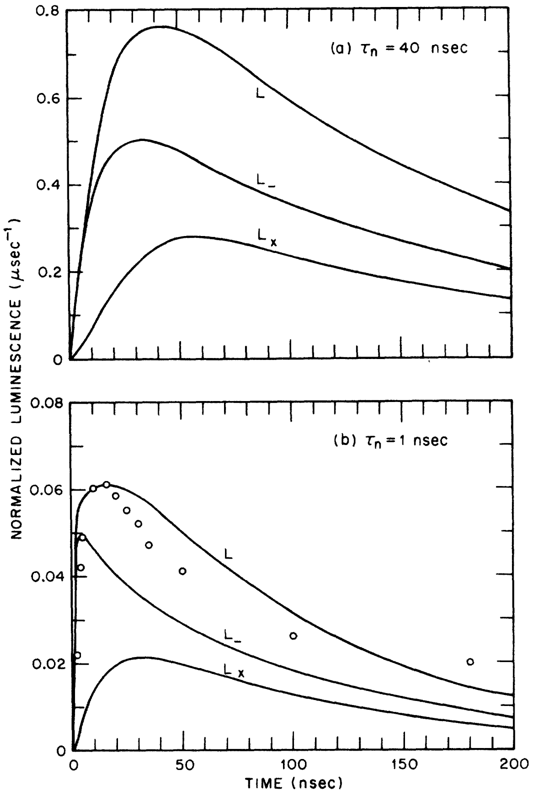

FIG. 4. Plots of the time dependence of the normalized red luminescence L/N [see Eqs. (35)–(37)] calculated for impulse-excitation conditions in GaP(Zn, O) using the parameters given in Table I and a net acceptor concentration $N_A = 10^{18}$ cm^{-3}. Shown is the total luminescence L and the components L_- and L_x computed for a shunt-path lifetime (a) $\tau_n = 40$ nsec and (b) $\tau_n = 1$ nsec. The open circles are taken from the results of the reversed-bias electroluminescence experiment in Ref. 10.

measuring minority-carrier lifetime. To determine the lifetime, it is necessary to fit the luminescence response to the theoretical expressions given above and adjust τ_n for a best fit. Note that when τ_n is long, the rise time is insensitive to τ_n, since $\tau_m \approx \tau_{nt}$ in this limit. On the other hand, when τ_n is short the rise time is controlled by τ_n since $\tau_m \approx \tau_n$. However, the amplitude of the luminescence drops in proportion to τ_n, making it more difficult to observe the luminescence time response. Because previous workers[10] only included the effects of the N_t^x luminescence in their analysis, they concluded that the rise time depends on the hole capture time τ_{pt}, and that by measuring the rise time when τ_m is short one should be able to obtain directly an experimental value for τ_{pt}. We believe that the results of our analysis make this point of view uncertain.

Finally, a comment is in order regarding the possibility of observing the predicted free-to-bound luminescence spectrally, as has been done recently,[21] for example, for the deep oxygen donor in GaP. In the latter case, a new no-phonon emission line was observed at 87 °K at an energy $\approx E_A + kT$ higher than the no-phonon donor-acceptor emission line, which dominates the infrared emission from oxygen at lower temperatures (E_A is the acceptor binding energy). By analogy, we would expect a new emission line at ~ 300 °K due to free-to-bound transitions from the Zn-O center in the red region of the spectrum at an energy $\approx E_h + kT$ higher than the excitonic recombination. However, even at very low temperatures the red excitonic emission is very broad and almost devoid of structure,[8] which seems to argue against observation of a new line at 300 °K. By contrast, the green emission from the nitrogen isoelectronic center in GaP shows sharp structure even up to room temperature.[22] From our calculations, one should expect a new free-to-bound line to appear at temperatures above ≈ 77 °K (see Fig. 2). In this case, however, structure in presently available luminescence data cannot be unambiguously identified because of the very strong self-absorption of the luminescence which is emitted at ~ 10 meV below the band edge. Indeed, we expect the predicted free-to-bound emission from nitrogen at 77 °K to peak in energy about 3 meV *above* the band edge, and consequently to be completely obscured by self-absorption. (In this sense the no-phonon free-to-bound emission would be effectively nonradiative.) The ideal candidate for spectral analysis would be an isoelectronic center which deeply traps a minority carrier, but binds the majority carrier with only ~ 10 meV. No such center has been identified for GaP.

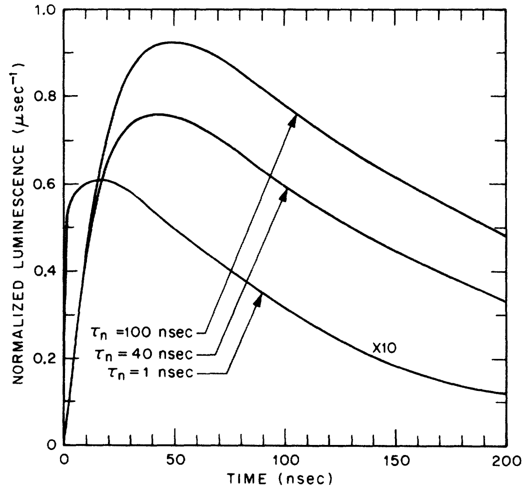

FIG. 5. The calculated impulse-excited time response of the red luminescence in GaP(Zn, O) for three values of shunt-path lifetime τ_n. Parameter values and normalization are the same as in Fig. 3. The $\tau_n = 1$-nsec curve has been magnified by a factor of 10.

V. CONCLUSIONS

This paper has introduced the importance, and possible dominance, of free-to-bound transitions from isoelectronic impurities in the high-temperature regime. We have shown that excitonic and free-to-bound transitions are due basically to recombination of trapped electrons, forming singly occupied (charged) states of the isoelectronic center, with bound and unbound holes. The electric dipole matrix element for the free-to-bound transition was shown to be enhanced appreciably by the Coulomb attraction of the singly charged state. Analytically the Coulomb attraction was accounted for by using Coulomb wave functions for the unbound hole state.

Previous work on recombination at isoelectronic Zn-O centers in GaP has assumed that the room-temperature emission was entirely due to excitons. The results of this paper provide evidence that free-to-bound recombination at Zn-O centers is an important and even dominant process. Theoretically, we calculated a free-to-bound lifetime of $\tau_{er} \approx 0.8$ μsec, and from experimental impulse data[10] we found $\tau_{er} \approx 1$ μsec. These values are in reasonable agreement.

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