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Transient characteristics of excitons bound at hole-attractive isoelectronic centers in GaP

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In this paper we present detailed luminescence-decay-time measurements of excitons bound at hole-attractive isoelectronic centers in GaP. We have found that the measured luminescence decay time can generally be explained with a model assuming full thermalization between the two lowest, singlet ($S=0$) and triplet ($S=1$), electronic levels of the bound exciton (BE). The values for the decay time of the dipole-forbidden triplet transition vary between 100 μs and 1 ms for the different bound excitons, while the allowed singlet transitions have decay times of a few microseconds. For some centers the effect on the decay time of the thermal quenching of the BE is considered, and we obtain good agreement for the value of the thermal activation energy, when compared with previous photoluminescence measurements. Different mechanisms for the interaction causing thermalization between the singlet and triplet are discussed. Also, the effect on the measured decay time due to thermalized or unthermalized magnetic sublevels in the triplet is discussed, and we conclude that at least one of the centers, the 1.911-eV bound exciton, has an unthermalized triplet level.

I. INTRODUCTION

In recent years a large number of neutral complex defects have been studied in GaP, particularly in samples doped with Cu, such as the COL,[1,2] 1.911 eV,[3,4] and Cu-C center.[5] Codoping with Li causes additional neutral complexes named (Cu-Li) centers, of which the most dominant ones are labeled $(\text{Cu-Li})_{\text{I}}$,[6] $(\text{Cu-Li})_{\text{II}}$,[6,7] $(\text{Cu-Li})_{\text{III}}$,[8] and $(\text{Cu-Li})_{\text{V}}$.[9] Similar centers are also obtained during codoping with Au and Li, the so-called (Au-Li) centers[10] numbered from 1 to 3. These centers have been studied via their bound-exciton (BE) recombination. Several optical techniques, including photoluminescence (PL), photoluminescence excitation (PLE), optically detected magnetic resonance (ODMR), and Zeeman measurements have been used to investigate the properties of the BE's and the corresponding centers. The atomic configurations of these centers is not well established, but all of them are believed to involve Cu on a Ga site, or Au on a Ga site for the (Au-Li) centers.

The electronic structure of the BE's associated with these defects is, on the other hand, rather well understood.[11] The classes of neutral defects discussed here are hole attractive, due to a dominantly hole-attractive impurity potential for the defects. The second particle, the electron, necessary to form a BE is bound to the hole by Coulomb interaction, according to the Hopfield-Thomas-Lynch (HTL) model.[12] It is assumed that the effect of the local strain around the defect is much stronger than the spin-orbit coupling, giving an orbitally nondegenerate spinlike ($s_h=\frac{1}{2}$) state as the lowest hole state. The spinlike hole is combined with a likewise spinlike electron ($s_e=\frac{1}{2}$) to form a BE with either a spin singlet ($S=0$) or a spin triplet ($S=1$) configuration, corresponding to antiparallel or parallel spins, respectively. For all these BE's the triplet state is at lower energy than the singlet state. The energy difference between the singlet and triplet ΔE_{st} is determined by the electron-hole exchange coupling, and is usually in the order of a few meV, but can also be as large as 23 meV for the COL and 90 meV for 1.911-eV BE. Some of the BE's, for example, for the $(\text{Cu-Li})_{\text{III}}$ and Cu-C centers, have been found to have an electronic structure consisting of two singlet-triplet (ST) pairs.[5,8] The recombination of a BE from a triplet state is a spin-forbidden transition, while the singlet state corresponds to an allowed transition. In practice this means that the transition probability of a triplet transition is much lower than the singlet transition, or that the triplet decay time is considerably longer than the corresponding decay time for the singlet.

The decay times of ST-pair BE's in GaP have previously not been studied in detail, but some scattered results have been published. The COL BE was reported to have a decay time of 100 μs at 4.2 K.[13] The $(\text{Cu-Li})_{\text{I}}$ BE was reported to have a decay time of 0.2 ms and 20 μs for the triplet and singlet, respectively.[14] These values were probably measured at only two different temperatures, where the respective transition is dominating, without considering the effects of thermal equilibrium between the levels. The value obtained at higher temperatures was then erroneously interpreted as the singlet decay time. Also values of 500 and 4 μs for the triplet and singlet transition, respectively, of the $(\text{Cu-Li})_{\text{III}}$ BE (Ref. 14) were obtained, without a proper model taking the temperature effects into account.

The need for a comprehensive treatment of the transient properties of the ST BE system, in connection with careful experimental data, is therefore apparent. In this paper we will present extensive temperature-dependent measurements of the decay time from a number of ST-pair BE systems in GaP. The result can in most of the cases be explained by a simple theoretical thermalization model presented below, and for the remaining cases plausible explanations for the discrepancies will be discussed.

The paper is organized in the following way. In Sec. II we present a simple theoretical model for the transient recombination of a ST pair. The experimental procedure about sample preparation and the measuring equipment are discussed in Sec. III. In the different parts in Sec. IV we present the experimental results obtained for different BE's, starting with the $(\text{Cu-Li})_{\text{I}}$ BE as the typical model system. The experimental results are discussed in Sec. V. Finally we summarize the most important conclusions in Sec. VI. Minor parts of the results presented in this paper have previously been published.[5,10,15]

II. SIMPLE THEORETICAL MODEL FOR THE TRANSIENT RECOMBINATION OF A SINGLET-TRIPLET PAIR

In order to explain the transitions from and within a two-level system, like the ST pair, we describe the population of each level, n_s and n_t, with two coupled rate equations,

$$n_t(t)=G_t(t)+W_{st}n_s(t)-W_{ts}n_t(t)-(W_{\text{th}t}+W_{Rt})n_t(t) \ , \tag{1}$$

$$n_s(t)=G_s(t)+W_{ts}n_t(t)-W_{st}n_s(t)-(W_{\text{th}s}+W_{Rs})n_s(t) \ , \tag{2}$$

where $G(t)$ is the generation rate caused by external excitation and W_R is the radiative recombination rate from each level. In this case the generation occurs with a fast pulsed laser and $G(t)$ is considered as a δ function at $t=0$. W_{ts} and W_{st} are relaxation rates, due to the spin-lattice interaction and spin-orbit mixing between the levels. W_{th} denotes transition rates for any thermally activated process removing population from the levels. This process can involve either thermal relase of the electron, of both the electron and the hole as free particles, or thermal release of the BE as an entity. Which of these processes dominates is determined by the relationship between the binding energy of the electron to the hole, binding energy of the hole to the defect, and activation energy for the thermal process. In any case we assume that the thermal process W_{th} is due to a single thermally activated process, which can be written as[16]

$$W_{\text{th}}=W_0\exp(-E_a/kT) \ , \tag{3}$$

where E_a is the activation energy and W_0 is assumed to be independent of temperature and of the order of the vibrational lattice frequency $10^{12}-10^{13}$ s^{-1}. Nonradiative Auger processes are assumed to be of no importance for these isoelectronic centers, since no third particle is present at the defect to participate in the Auger process. We are also assuming here that BE transfer to or from other defect complexes is of negligable importance, although in practice such processes might occur.[17]

The combined rate

$$T_1=\frac{1}{W_{ts}}+\frac{1}{W_{st}} \tag{4}$$

defines the rate at which the population of the total system approaches thermal equilibrium. If this rate is larger than any of the radiative recombination rates involved, the singlet and triplet levels can be considered to be in thermal equilibrium at all times after excitation. The BE's are then canonically distributed amonst the levels according to

$$\frac{n_s}{n_t}=g\exp(-\Delta E_{st}/kT) \ , \tag{5}$$

where g is the degeneracy ratio between the singlet and triplet levels, $g=g_s/g_t=\frac{1}{3}$. Because of this coupling between the two levels the experimentally measured decay time will be the same irrespective of which transition is detected. The solution to the rate equations under these assumptions gives the following expression for the experimentally observed decay time:

$$\begin{aligned}\tau_{\text{expt}}&=\frac{1}{W_{\text{expt}}}\\&=\frac{1+g\exp(-\Delta E/kT)}{W_{Rt}+W_{\text{th}}+(W_{Rs}+W_{\text{th}})g\exp(-\Delta E/kT)} \ .\end{aligned} \tag{6}$$

A simpler form of this equation, without the thermal part W_{th}, has previously been used to describe measured BE decay times from a two-level system in Si,[18,19] and for the BE associated with the electron-attractive isolated nitrogen defect in GaP.[20] Equation (6) can be generalized to describe the decay from any thermalized many-level system,

$$\tau_{\text{expt}}=\frac{\sum_i g_i\exp(-\Delta E_i/kT)}{\sum_i[W_{Ri}+W_{\text{th}}(E_i)]g_i\exp(-\Delta E_i/kT)} \ , \tag{7}$$

where the summation is over all i levels, and ΔE_i is the energy difference between the ith level and the lowest level, $i=1$. This equation is used, e.g., to describe the decay from a BE with a double TS-pair electronic structure.

III. EXPERIMENT

A. Sample preparation

The copper-related defects giving rise to the COL and the 1.911-eV BE's were produced by using nominally undoped epitaxial layers as starting material. The Cu diffusion was made at temperatures in the range of 900–1100 °C, followed by a rapid cooling in water to room temperature. Both the COL and the 1.911-eV emissions were present in the same samples.

The different Cu-Li centers were produced in a two-step diffusion procedure. The first step, which involved Cu diffusion, was made in the same way as described above for the COL and 1.911-eV defects. However, epitaxial layers as well as bulk material were used as starting material. The second step involves Li diffusion in the temperature range from 400 to 1000 °C during 40 min to 4 h. The $(\text{Cu-Li})_{\text{I}}$ emission is strongest in solution grown material. In epitaxial material $(\text{Cu-Li})_{\text{I}}$, $(\text{Cu-Li})_{\text{II}}$, and $(\text{Cu-Li})_{\text{III}}$ are present with high luminescence efficiency. The $(\text{Cu-Li})_{\text{V}}$ emission is relatively strongest in bulk material and is always accompanied by the $(\text{Cu-Li})_{\text{III}}$ emission. The initial COL and 1.911-eV emissions are never present after Li diffusion. Cu-C centers are produced from C-rich solution grown material, with Cu diffused as described above. The Cu-C centers are formed at a second diffusion step at about 900 °C during 1 h. The Au-Li centers were produced with epitaxial layers, where the Au diffusion was done first at 800 °C during 1 h, followed by a Li diffusion at 400 °C, but during longer times. The produced samples appear to have some contamination of Cu, since both the $(\text{Cu-Li})_{\text{II}}$ and $(\text{Cu-Li})_{\text{III}}$ spectra are also observed in these samples.

B. Experimental procedure

The decay measurements were done with a pulsed nitrogen laser together with a dye-laser system. The dye laser was producing pulses with 7-ns pulse width and 100-Hz repetition rate. The photon energy was usually 2.41 eV and the maximum average power was 50 mW. If sample heating was observed to affect the measurements, neutral density filters were used to decrease the laser excitation intensity. The samples were placed in a combined bath and flow He cryostat, in which the temperature could be regulated between 1.5 K up to room temperature. At temperatures below 4.2 K the samples were immersed into liquid He and at higher temperatures the samples were surrounded by a He-atmosphere at normal pressure. The luminescence from the samples was focused into a 0.65-m double monochromator and detected with a cooled GaAs photomultiplier tube (PMT). The signal from the PMT was amplified and measured with a transient recorder (BIOMATION model 6500). A computer system was used to perform signal averaging of the signal measured by the transient recorder and to evaluate the final decay curves.

IV. EXPERIMENTAL RESULTS

A. The $(\text{Cu-Li})_{\text{I}}$ BE

The BE best described by the model presented in the previous chapter is the $(\text{Cu-Li})_{\text{I}}$ BE, which has the triplet PL line at 2.3062 eV and an electron-hole exchange interaction of $\Delta E_{st} = 1.0$ meV. Furthermore, the $(\text{Cu-Li})_{\text{I}}$ BE has no overlapping emissions, which otherwise can complicate the measurements and their interpretation. The decay of the $(\text{Cu-Li})_{\text{I}}$ BE and most of the other ST-pair BE's are typically exponential, as shown in Fig. 1, although we have observed a nonexponential decay at low temperatures and high excitation intensities. This nonexponential behavior consists of a faster decay during the first few microseconds after the laser excitation, followed by a slower and exponential decay at longer times after excitation, Fig. 2. We believe that this faster decay is mainly due to sample heating and other noncontrollable effects caused by high excitation.[15] This effect is successively reduced with decreased laser excitation intensity and all decay measurements presented in this paper are done with reduced laser intensity to avoid this situation.

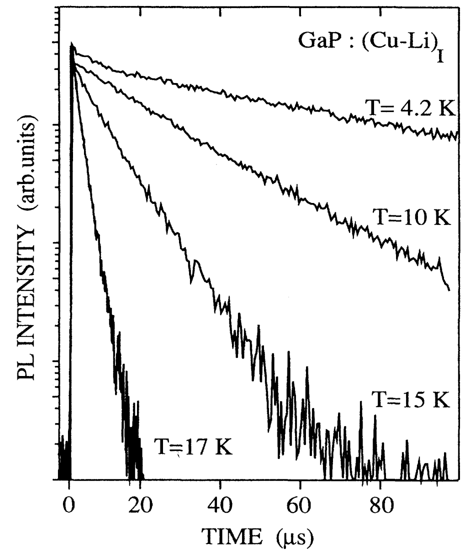

FIG. 1. PL intensity (log scale) vs time after laser excitation of the $(\text{Cu-Li})_{\text{I}}$ BE at four different temperatures. The decay curves are exponential at all temperatures corresponding to a decay time of 68, 26, 8.6, and 1.8 μs for 4.2, 10, 15, and 17 K, respectively.

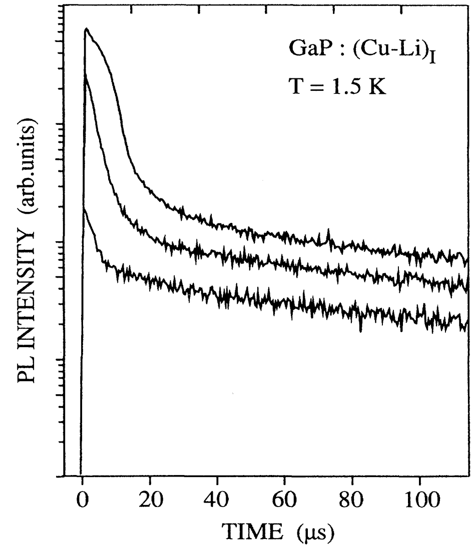

FIG. 2. PL decay of the $(\text{Cu-Li})_{\text{I}}$ BE for three different excitation intensities. From top to bottom the average excitation intensity was 3, 0.6, and 0.18 mW. The nonexponential decay during the first microsecond is believed to be due to temperature effects and effects caused by nonequilibrium conditions during the laser excitation.

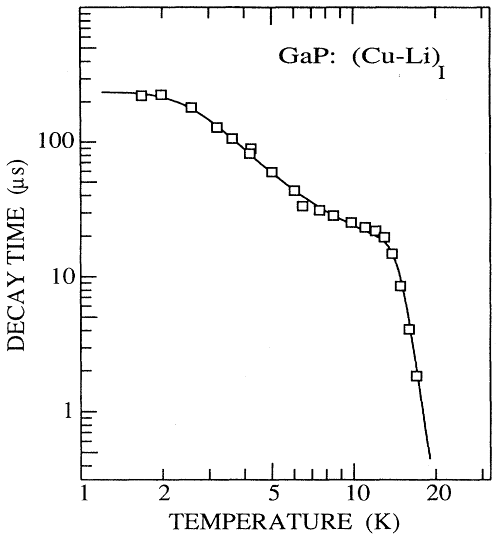

FIG. 3. Measured decay time of the (Cu-Li)$_I$ BE in GaP as a function of temperature. The squares correspond to the experimental values while the solid line represents the best fit to the experimental data using Eq. (6). The best fit parameters are $\tau_t = 235$ μs, $\tau_s = 2.5$ μs, and the thermal activation energy $E_a = 22.5$ meV.

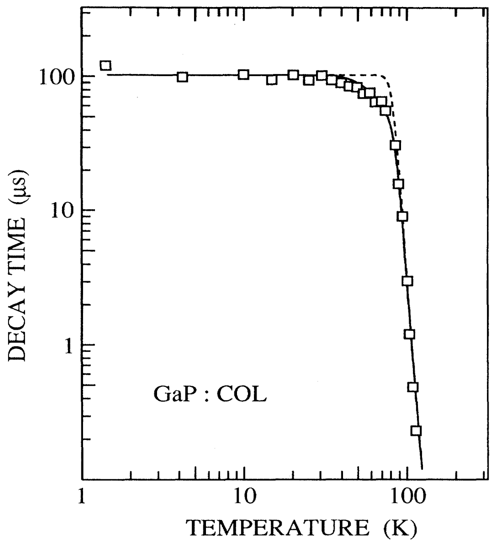

FIG. 4. Decay time vs temperature for the COL BE recombination. The measured decay time at lower temperatures corresponds to the triplet decay time $\tau_t = 100$ μs. The allowed singlet transition rarely influences the total recombination because of the large singlet-triplet splitting $\Delta E_{st} = 23.2$ meV. The solid line is the best fit to Eq. (1) neglecting the singlet transition, while the dotted line is the same fitting with the singlet included. The value for the singlet was in this case $\tau_s = 1.1$ μs. The thermal activation energy causing the fast decrease in decay time at ~90 K was found to be 150 meV.

The measured decay time as a function of temperature is shown in Fig. 3. The detection was in this case made over an energy region including both the singlet and triplet no-phonon lines. At low temperatures the triplet level is strongly thermally favored and the measured decay time is very close to the triplet radiative decay time. When the temperature is increased a larger number of BE's will be in the singlet level and the measured decay time is decreased due to the lower value of the singlet radiative decay time. The measured decay time will ideally approach the value $4\tau_s$ when the temperature goes to infinity. This is not happening for the (Cu-Li)$_I$ BE, however, since the BE is thermally quenched at about 15 K when the measured decay time decreases rapidly, as can be seen in the figure.

A fitting of the experimental values with Eq. (6) gives a very good agreement, as shown by the solid line in Fig. 3. The best fit was obtained with $\tau_t = 235$ μs, $\tau_s = 2.5$ μs, and $E_a = 21.5$ meV. The activation energy is comparable to the energy difference between the free exciton[13] (FE) and the (Cu-Li)$_I$ Be, i.e., 2.3284−2.3072 eV=21.2 meV. The thermal activation energy is thus interpreted as a thermal release of the BE as an entity from the defect into an FE.

B. The COL BE

The electron-hole exchange interaction of 1.0 meV for the (Cu-Li)$_I$ BE is the smallest splitting for all ST BE's studied in detail in GaP. The COL BE at 2.1774 eV (Ref. 1) has a quite large splitting between the singlet and the triplet $\Delta E_{st} = 23.2$ meV, and the temperature dependence of the BE decay time is expected to be totally different compared to (Cu-Li)$_I$ recombination. The experimentally determined decay time of the COL BE is shown in Fig. 4. As predicted from Eq. (6) the decay time is constant at temperatures up to ~50 K due to the fact that the triplet is strongly thermally favored at these temperatures. At ~50 K the measured decay time is slightly decreased due to the thermal interaction between the singlet and triplet levels, and at ~90 K strongly decreased due to thermal quenching of the BE.

The solid line corresponds to the best fit of the experimental data to Eq. (6), where the parameters for best fit are $\tau_t = 100$ μs, $\tau_s = 1.1$ μs, and $E_a = 152$ meV. It should be noticed, however, that we have neglected all temperature-dependent processes that may influence the radiative transition probabilities, W_{Rs} and W_{Rt}, such as the strong phonon coupling observed in the COL spectrum. Therefore the value obtained for the decay time of the singlet recombination should not be taken too literally. As a comparison the expected temperature dependence of the decay time assuming no interaction between the singlet and the triplet is inserted into Fig. 4, represented by a dotted line. The value obtained for the thermal activation energy is in good agreement with the previous obtained value $E_a = 153$ meV (Ref. 2) from normal measurements of thermal quenching of the photoluminescence intensity. This value is comparable to the binding energy of the BE if this is defined as the energy difference between the FE and the BE, $E_b = 151$ meV.

C. The 2.238-eV Cu-C BE

An intermediate case regarding the electron-hole exchange splitting can be found for the (Cu-C) BE at 2.2383 eV.[5] The electronic structure of the (Cu-C) BE is more complicated, compared to the previously mentioned cases, consisting of two singlet-triplet pairs, where the two triplets at lower energy are separated by 0.9 meV and the exchange splitting is 8.0 meV for both pairs. The singlet and triplet PL lines can easily be resolved spectrally, making it possible to measure the time decay from the singlet and triplet levels separately. Furthermore, both the triplet and the singlet recombination occur with comparable intensities in luminescence at temperatures above ~25 K, due to the relatively large electron-hole exchange splitting. Figure 5 shows the temperature dependence of the decay time where the squares correspond to detection at the two triplets, while the triangles indicate values obtained for detection on the singlet recombination. This apparently equivalent result is expected from the model, and is another piece of evidence for a strong thermalization between the singlet and the triplet levels. The solid line in Fig. 5 corresponds to the best fit obtained with Eq. (7), including two singlet and two triplet levels but disregarding the thermal quenching of the BE in Eq. (7). Best fit is obtained with different decay times for the two triplets 140 and 74 μs, and 0.8 and 2.0 μs for the singlet levels, respectively.

D. The $(\text{Cu-Li})_{\text{II}}$ and $(\text{Au-Li})_{\text{I}}$ BE's

Figure 6 shows the decay time of the $(\text{Cu-Li})_{\text{II}}$ BE as a function of temperature. At low temperatures this emission is dominated by a transition at 2.2758 eV, while a transition at 1.9 meV higher energy dominates at higher temperatures. This BE has never been studied in detail previously, but the PL spectrum is published[6,7] and was interpreted as an ST pair with an electron-hole exchange splitting of $\Delta E_{st} = 1.9$ meV. It is not possible to obtain a good fit to the experimental data using this splitting, however. The best fit is instead achieved with a much smaller splitting of $\Delta E_{st} = 0.7$ meV. Based on this result we suggest an alternative interpretation of the $(\text{Cu-Li})_{\text{II}}$ BE electronic structure which would consist of two singlet-triplet pairs, similar to the case of the (Cu-C) BE described above. The energy splitting between the singlet and triplet is assumed to be 0.7 meV, while the energy difference between the two pairs is 1.9 meV. With this electronic structure the singlet transitions will dominate the observed luminescence at all temperatures above 2 K. PL measurements of the relative intensity of the two observed lines as a function of temperature support this interpretation, since the ratio of the respective recombination rates is close to unity. This can also be seen in the original data,[7] comparing the intensity ratio between the lines at different temperatures. In the original low-temperature spectrum it is also possible to see a small

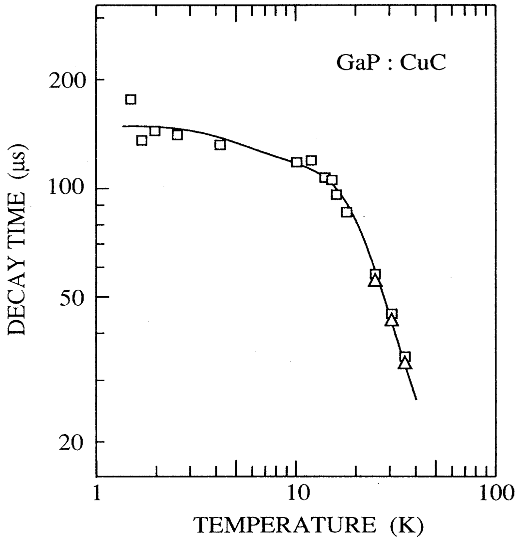

FIG. 5. Temperature dependence of the Cu-C BE decay. The squares are measured with detection at the triplet emission while the three triangles at 25, 30, and 35 K are measured at the singlet emission. The similarity of the resulting values at the two measurements supports the model of strong thermalization between the singlet and triplet levels. The solid line represents the best fit to Eq. (7) using four levels to explain the double TS-pair electronic structure. The best fits were obtained with $\tau_{t1} = 147$ μs, $\tau_{t2} = 75$ μs, $\tau_{s1} = 0.8$ μs, and $\tau_{s2} = 2.1$ μs. The decay is mostly influenced by the values of the lower energy TS pair, denoted as $t1$ and $s1$.

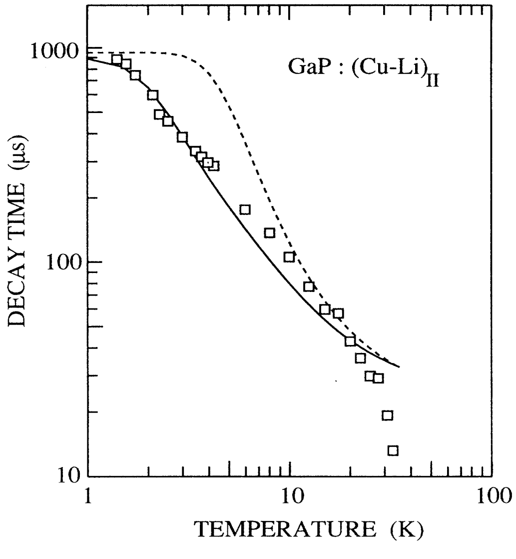

FIG. 6. Temperature dependence of the $(\text{Cu-Li})_{\text{II}}$ BE decay. The dotted line shows the expected curve with the originally proposed TS-pair electronic structure. The solid line is the best fit obtained with the four-level model of Eq. (7) corresponding to a double TS-pair electronic structure. The best fit was obtained with $\tau_{t1} = \tau_{t2} = 870$ μs, $\tau_{s1} = 15$ μs, and $\tau_{s2} = 3.5$ μs. The fit was relatively independent of the value of τ_{t2} and the two triplet transitions were forced to have the same decay time in the fitting procedure. The decrease of the decay time at 30 K, due to the thermal quenching of the BE, is not included in the fitting equation.

TABLE I. Summary of energies and measured decay times of different BE emissions in GaP. E_a is the activation energy for thermal quenching of the BE luminescence calculated from the decrease in measured decay time vs temperature. Values in parentheses are considered not to have a high accuracy, as described in the text.

BE	Triplet energy (eV)	ΔE_{st} (meV)	τ_t (μs)	τ_s (μs)	E_a (meV)
$(\text{Cu-Li})_{\text{I}}$	2.3026	1.0	235	2.25	23.8
$(\text{Cu-Li})_{\text{II}}$	2.2758	0.7	870	15	
	2.2777	0.7	(870)	(3.5)	
$(\text{Au-Li})_{\text{I}}$	2.256	0.6	600	18	
	2.258	0.6			
$(\text{Cu-Li})_{\text{III}}$	2.2419	2.1	1800	1.2	
	2.2430	2.4	(74)	(32)	
Cu-C	2.2383	8.0	145	0.8	
	2.2392	8.2	(74)	(2.0)	
$(\text{Au-Li})_{\text{II}}$	2.206	2.6	1240	1.9	
$(\text{Cu-Li})_{\text{V}}$	2.172	2.0	73		
COL	2.1774	23.2	100	1.1	152
$(\text{Au-Li})_{\text{III}}$	2.156	3.0	700		
1.911	1.911	90.0	95		140

shoulder on the low-energy side of the two intense lines, which possibly is due to triplet recombination. Zeeman measurements also confirm the identification of the two PL lines as singlets, since no splitting is observed at magnetic fields up to 6 T. Even if the two triplet levels are seen very weakly in luminescence they are strongly affecting the time decay of the total luminescence connected to the $(\text{Cu-Li})_{\text{II}}$ BE. The solid line in Fig. 6 corresponds to a fit using a four-level model according to Eq. (3). The best fit is obtained with $\tau_{t1}=\tau_{t2}=870$ μs, $\tau_{s1}=15$ μs, and $\tau_{s2}=3.5$ μs. The two triplet transitions are forced to be equal during the fitting, since the value of τ_{t2} has a very small influence on the decay curve. The decrease of the decay time at temperatures above 25 K is due to thermal excitation of the BE, but this effect was not included in the fitting equation.

The $(\text{Au-Li})_{\text{I}}$ BE (Ref. 10) has the same PL and time-decay characteristic as the $(\text{Cu-Li})_{\text{II}}$ Be, and we propose that the $(\text{Au-Li})_{\text{I}}$ has an electronic structure similar to that of $(\text{Cu-Li})_{\text{II}}$. The energies and time decay constants for this BE together with all other excitons mentioned in this paper are summarized in Table I.

E. The 1.911-eV BE

The luminescence decay of the 1.911 eV BE recombination exhibits a completely different structure than the previously mentioned cases. While these have a good exponential decay curve the 1.911 eV BE has a nonexponential decay, as can be seen in Fig. 7. It is possible to deconvolute the decay curve into two exponential curves, as indicated in Fig. 7 by the two straight lines. A time-resolved spectral measurement using a boxcar technique shows that the fast and slow components have the same spectral dependence, and can consequently be attributed to the same recombination center. The ratio of the integrated intensity of the two components is close to unity at temperatures below 60 K. At higher temperatures the slower component disappears and the total decay is single exponential, consisting of the fast component only. The decay times of the two components as a function of temperature are shown in Fig. 8. The decay time of the fast component is 40 μs at 1.5 K and increases to reach a value of 80 μs at 30 K. This increase in decay time is not seen for any other BE and is not possible to explain within the model of Eq. (6). The decay time is expected to be constant in the temperature region below 80 K since the singlet level can be totally neglected, due to the

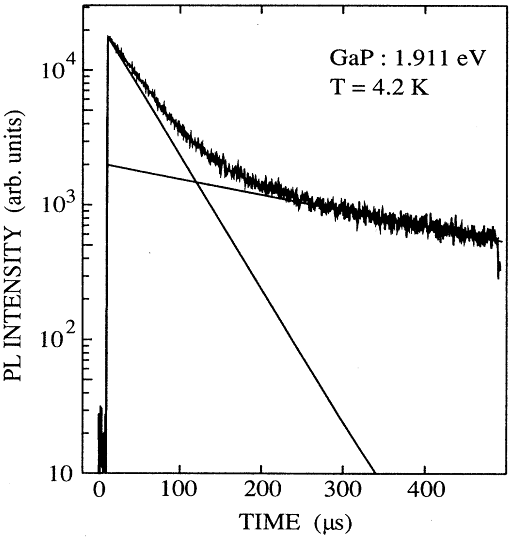

FIG. 7. A typical decay curve of the 1.911 eV BE recombination at 4.2 K. The decay can be convoluted into two exponential curves as indicated in the figure. The fast component corresponds to a decay time of $\tau=43.6$ μs while the slower component decays with $\tau=370$ μs.

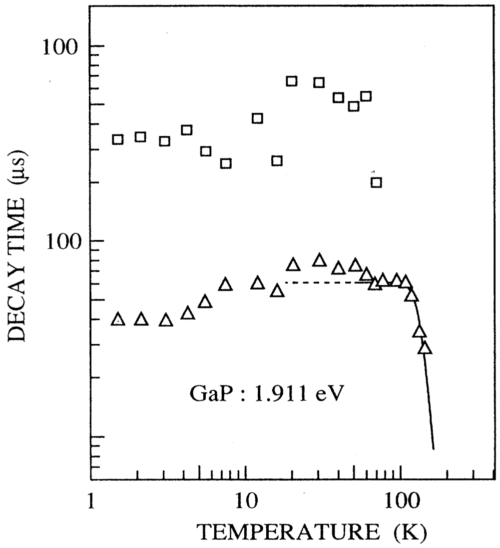

FIG. 8. Deconvoluted decay times of the 1.911 BE. The squares correspond to the fast component which is considered to be the main decay. The different components are interpreted as being due to recombination from different nonthermalized triplet sublevels. The increase of the fast components decay time with increased temperature up to 30 K is not expected from the model. The decrease above 100 K is predicted and corresponds to thermal quenching of the BE with an activation energy of 140 meV, as shown by the dotted line.

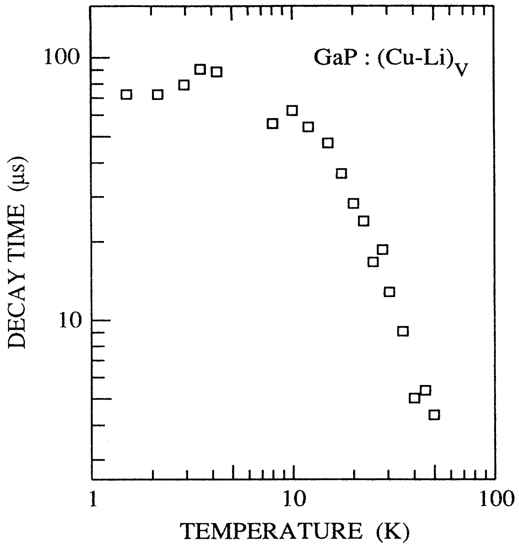

FIG. 9. Temperature dependence of the decay time of the (Cu-Li)$_V$ BE. The measured decay curve has an additional slow component which is assumed not to be related to the (Cu-Li)$_V$ Be. The curve in the figure is not possible to explain with the model presented in Eq. (6). The decay time for the triplet is, however, estimated by interpolation at low temperatures to have a value of 73 μs.

extremely large electron-hole exchange splitting $\Delta E_{st} = 90$ meV in this case. The decrease in decay time above 80 K, due to the thermal quenching of the BE, is, however, expected. The dotted line is a fitting to Eq. (6) of the experimental values at temperatures above 65 K. The best fitting was obtained with $E_a = 140$ meV, which can be compared to the value obtained with PL measurements,[3] $E_a = 120$ meV. We suggest that the two components of the decay are due to recombination from different sublevels inside the triplet state. In contrast to the previous cases these sublevels seem to be nonthermalized. This effect will be discussed more in Sec. V.

F. The (Cu-Li)$_V$ BE

The (Cu-Li)$_V$ BE recombination spectrum exhibits a nonexponential decay similar to that of the 1.911 eV BE. The experimental situation is a bit more complicated, however, since the broad phonon wing of the (Cu-Li)$_{III}$ emission overlaps with the (Cu-Li)$_V$ emission. Furthermore, both of these emissions are believed to have a superimposed background consisting of the phonon coupling of the so-called 2.25 eV BE,[21] observed in ODMR experiments.

The decay of the (Cu-Li)$_V$ BE is also possible to deconvolute into two exponential decays. The fitting is, however, not satisfactory at low temperatures. The slower component, which has a decay time in the order of 200–400 μs, is believed to be due to background emissions not related to the (Cu-Li)$_V$ BE. It is not possible to exclude any transitions from different triplet sublevels, as observed for the 1.911 eV BE, since we have not been able to spectrally resolve the two components. The intensity of the slower component is reduced with increased temperature and disappears completely at about 30 K. The decay of the fast component, which is believed to be the main decay from the (Cu-Li)$_V$ BE, is shown as a function of temperature in Fig. 9. Separate measurements with detection in the singlet and triplet transitions give an identical decay curve over the entire time region, including both the fast and the slow component, respectively. The temperature dependence shown in Fig. 9 is not possible to explain with the presented model [Eq. (6)].

G. The (Au-Li)$_{II}$ and (Cu-Li)$_{III}$ BE's

Finally, we have measured the decay characteristics of two BE's which are good examples of a thermalized BE system as described by the presented model.

The (Au-Li)$_{II}$ BE has its lowest component at 2.206 eV and an exchange splitting of 2.6 meV.[10] The temperature dependence of the measured decay time is shown in Fig. 10. Because of overlapping emissions it was not possible to measure the decay in the temperature region where the thermal quenching process W_{th}, becomes important. The fittings of the experimental values were consequently done neglecting this part in Eq. (6). The values are in very good agreement with the thermalization model, as indicated with the solid line in Fig. 10. Best fit was obtained with $\tau_t = 1235$ μs and $\tau_s = 1.9$ μs for the triplet and singlet, respectively.

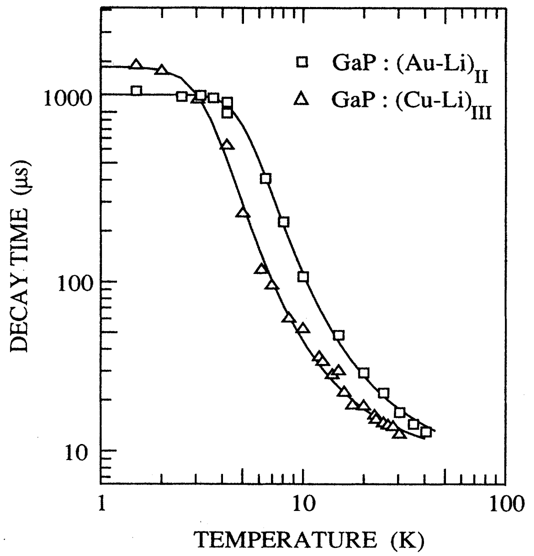

FIG. 10. Decay time of the (Cu-Li)$_{III}$ and (Au-Li)$_{II}$ BE's as a function of temperature. The (Cu-Li)$_{III}$ BE has a double TS-pair electronic structure and the solid line represents the fitting to the data using a four-level model according to Eq. (7), neglecting the temperature quenching part W_{th}. The best fit was obtained with $\tau_{t1}=1800$ μs, $\tau_{t2}=75$ μs, $\tau_{s1}=1.15$ μs, and $\tau_{s2}=31$ μs. For the (Au-Li)$_{II}$ BE good fitting was obtained using Eq. (6) with $\tau_t=1240$ μs and $\tau_s=1.9$ μs.

The decay of the (Cu-Li)$_{III}$ BE has also overlapping emissions giving a nonexponential decay. The dominating component can easily be evaluated from the total decay curve and is attributed to the (Cu-Li)$_{III}$ emission. The residual part of the decay, whose intensity is sample dependent, is believed to be due to emission from the 2.25 eV BE. The decay as a function of temperature is shown in Fig. 10. Best fit with a four-level model was obtained with $\tau_{t1}=1800$ μs, $\tau_{t2}=74$ μs, $\tau_{s1}=1.15$ μs, and $\tau_{s2}=32$ μs. As mentioned before the values for the higher energy pair, $t2$ and $s2$, have a very small influence on the fitting and the estimated values for these data are less accurate.

V. DISCUSSION

A. Thermalization properties of the BE's

When discussing the problem of thermalization between the different energy levels it is important to distinguish between the two different energy-level systems involved in the ST-pair exciton. The first system, which is most important in this study, is the singlet and triplet levels, and the thermalization between them governs the measured decay time for the excitons, as discussed in Sec. II. The second system concerns thermalization between the three magnetic sublevels inside the triplet. This has so far been neglected but all equations obtained in Sec. II assume that all three sublevels are thermalized.

The experimentally observed thermalization between the singlet and triplet levels can be explained by relaxation caused by different coupling mechanisms. With a spin-orbit interaction it would be possible to couple the singlet level with one of the triplet sublevels. This mechanism is important in singlet to triplet relaxations in molecular crystals but is generally not believed to be the dominating mechanism for the ST BE since it requires mixing with excited states of the hole, at higher energies. Another possible mechanism is interaction between the triplet and singlet via a weak phonon coupling.[22] The relaxation time in a similar system, the exciton bound at isolated N_P in GaP, has previously been reported to be 25 ps.[23] The exciton is in this case electron attractive and the relaxation occurs from the $J=1$ level down to the $J=2$ level. To explain the fast relaxation they concluded that the relaxation mechanism involved a lattice-orbit coupling. The corresponding relaxation time for the ST system has not been measured, but is assumed to be of the same order of magnitude, to explain the observed thermalization. It is not possible to say which mechanism is most important in our case, but in all cases the coupling will cause a mixing of the singlet and the triplet state, explaining the finite radiative recombination time observed for the originally forbidden triplet transition. The opposite process, i.e., transfer from triplet to singlet (W_{ts}), is at thermal equilibrium related to the singlet triplet transfer rate (W_{st}) as

$$\frac{W_{ts}}{W_{st}}=\frac{g_s}{g_t}\exp(-\Delta E/kT) . \qquad (8)$$

Using $\Delta E=1.0$ meV, which is the ST splitting for (Cu-Li)$_I$, and the value of 25 ps for the singlet-triplet relaxation time we obtain from Eqs. (8) and (4) a value of $T_1=15$ ns, as the time at which the system approaches equilibrium at the temperature 2 K. This value is well below the radiative recombination times involved and the system is then expected to reach and maintain thermal equilibrium, between the singlet and triplet, during the time the PL decay is measured.

The problem associated with thermalized or unthermalized triplet sublevels has recently been discussed in detail.[24] In this paper we will only discuss the effects on the measured decay times for the different cases that arise. The model presented in Sec. II assumes that all sublevels are thermalized. The relative population of states between the sublevels will then be the same and close to unity at all temperatures, due to the small zero-field splitting. The obtained values for the triplet decay time are interpreted as an effective decay time given by

$$\tau_t=\left[\frac{1}{\tau_{t0}}+\frac{1}{\tau_{t+}}+\frac{1}{\tau_{t-}}\right]^{-1}=\left[\frac{1}{\tau_{t0}}+\frac{2}{2_{t\pm}}\right]^{-1} , \qquad (9)$$

since $\tau_{t+}=\tau_{t-}=\tau_{t\pm}$, where τ_{t0}, τ_{t+}, and τ_{t-} corresponds to the decay time for the different sublevels, respectively.

If, on the other hand, the sublevels are unthermalized the situation is more complicated. In this case the singlet can be in thermal equilibrium with only one of the different triplet sublevels. The degeneracy of the triplet level will be lowered and should be put equal to 1 in Eqs. (6) and (7). It should be noted that it is very difficult from the decay measurements to distinguish between the fully thermalized case and the above case with unthermalized sublevels and thermal equilibrium between the singlet and only one of the triplet sublevels. Evaluation of the data above assumes the former case with the degeneracy $g=\frac{1}{3}$.

The 1.911-eV BE is the only BE in this study where we have observed any effect of an unthermalized triplet. This is seen via the doubly exponential decay observed, which is attributed to recombination from two different triplet sublevels. This has also been confirmed by microwave-induced delayed phosphorescence (MIDP),[25] where two different decay times associated with different sublevels were observed. The values obtained in MIDP is almost identical to the values obtained in this study. The 1.911 eV BE represents a case where both the triplet sublevels and the singlet-triplet system are unthermalized, due to the large exchange interaction of 90 meV for this BE. It is reasonable to suggest that the absence of interaction between the triplet and singlet is one possible explanation for the unthermalized nature of the triplet level.

B. Comparison with other BE systems

The obtained values of the singlet and triplet decay time for the different BE's in this study are summarized in Table I. The decay time of the triplet transition is assumed to be the most accurate one since it can be measured separately at low temperatures. The accuracy of the singlet decay time is strongly varying between the different BE systems, depending on the relationship between ΔE_{st} and E_a and the existence of overlapping emissions disturbing the decay measurements. The success of the fitting is less accurate for the cases where the four-level model is used, particularly, the values obtained for the higher-energy pair are uncertain, since their influence of the measured decay time is small. These values are given in parentheses in Table I.

It is interesting to note the similarity between the values of the $(\text{Cu-Li})_{\text{II}}$ and $(\text{Au-Li})_{\text{I}}$ BE's, which are assumed to have similar electronic structure. The values of the singlet decay time for these two centers are exceptionally high, 15 and 18 μs, respectively. It is reasonable to assume that the isoelectronic complex defect has the same configuration in these cases, differing only in having either a Au or Cu atom on a Ga site, as previously suggested.[8,10] For all other singlets the decay time is around a few microseconds, with a factor of 100–1000 difference between the allowed and forbidden transition.

The oscillator strength of the transition can be calculated from the decay time according to[19]

$$f=\frac{2\pi e m^{*} c^{3} h^{2}}{n e^{2} E^{2} \tau}\,, \tag{10}$$

where E is the recombination energy, τ is the decay time, n is the refractive index, with the other variables having their conventional notation. Using the free-electron mass we obtain a value in the order of 1×10^{-3} for the singlet transitions. This result is comparable to the values obtained in two different singlet-triplet systems in silicon.[19] In the so-called Q and S system the ratio between the forbidden and allowed transition was reported to 120 and 400, respectively, which is in the same order of magnitude as for our measurements in GaP.

The value of 10^{-3} for the oscillator strength of the GaP singlet BE transition is more than one order of magnitude lower than values obtained for the allowed transitions in electron-attractive BE systems in GaP. The decay time of the $J=1$ transition has been reported to 40, 70, and 100 ns for the N, Li-Li-O, and Zn-O BE's, respectively. This difference between hole- and electron-attractive defects can be explained as due to "band-structure enhancement" effect on the oscillator strengths for electron-attractive defects. The localized potential may in this case give rise to a bound electron wave function of a considerable extent in the Brillouin zone, and a strong mixing with other components, e.g., Γ can occur. The overlap with the hole wave function from the valence-band maximum is then increased and will strongly enhance the BE oscillator strength. This effect will not occur for BE's bound at hole-attractive defects.

VI. CONCLUSIONS

It is demonstrated in this work, covering a large number of singlet-triplet bound exciton systems in GaP, that the photoluminescence decay of these BE's are in general described by a simple model for a thermalized singlet-triplet system in which case a temperature-dependent single exponential decay rate is observed. These experimental data also indicate that the triplet sublevels are thermalized and that transfer effects to (or from) other defects can be neglected.

An exception from this picture is found for the 1.911-eV BE, where a nonthermalized triplet is concluded, probably due to the unusually large ST (exchange) splitting of 91 meV. Other deviations from this simple model of the observed decay rates are explained as due to interference of overlapping photoluminescence signals from other defects than the one under study.

This work provides a general background to the carrier kinetics in isoelectronic defects in GaP, together with previous work on electron-attractive such defects, in particular, the *N*-related centers. Future more-detailed spin-dependent experiments are of interest to explore the kinetics of carrier relaxation during the capture process of a BE to such defects. Techniques to perform such experiments for these ST-pair BE's are now under development.

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[1] B. Monemar, H. P. Gislason, P. J. Dean, and D. C. Herbert, Phys. Rev. B **25**, 7719 (1982).

[2] H. P. Gislason, B. Monemar, P. O. Holtz, P. J. Dean, and D. C. Herbert, J. Phys. C **15**, 5467 (1982).

[3] H. P. Gislason, B. Monemar, P. J. Dean, D. C. Herbert, S. Depinna, B. C. Cavenett, and N. Killoran, Phys. Rev. B **26**, 827 (1982).

[4] W. M. Chen, B. Monemar, H. P. Gislason, M. Godlewski, and M.-E. Pistol, Phys. Rev. B **37**, 2558 (1988).

[5] H. P. Gislason, B. Monemar, P. Bergman, and M.-E. Pistol, Phys. Rev. B **38**, 5466 (1988).

[6] H. P. Gislason, B. Monemar, M.-E. Pistol, P. J. Dean, D. C. Herbert, A. Kanaáh, and D. C. Cavenett, Phys. Rev. B **31**, 3774 (1985).

[7] H. P. Gislason, Ph. D thesis, University of Lund, 1981.

[8] H. P. Gislason, B. Monemar, M.-E. Pistol, P. J. Dean, D. C. Herbert, S. Depinna, A. Kanaáh, and B. C. Cavenett, Phys. Rev. B **32**, 3958 (1985).

[9] H. P. Gislason, B. Monemar, M.-E. Pistol, A. Kanaáh, and B. C. Cavenett, Phys. Rev. B **33**, 1233 (1986).

[10] P. Bergman, Q. X. Zhao, B. Monemar, and M.-E. Pistol, Mater. Sci. Forum **38-41**, 911 (1989).

[11] B. Monemar, U. Lindefelt, and W. M. Chen, Physica B+C **146B**, 256 (1987).

[12] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[13] R. G. Humphreys, U. Rössler, and M. Cardona, Phys. Rev. B **18**, 5590 (1978).

[14] A. Kanaáh, B. C. Cavenett, H. P. Gislason, B. Monemar, and M.-E. Pistol, J. Phys. C **19**, 1239 (1986).

[15] P. Bergman and B. Monemar, J. Lumin. **38**, 87 (1987).

[16] M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).

[17] W. M. Chen, M. Godlewski, P. Bergman, Q. X. Zhao, and B. Monemar, in *Proceedings of the Nineteenth International Conference on the Physics of Semiconductors, Warsaw, 1988,* edited by W. Zawadzki (Institute of Physics, Polish Academy of Science, Warsaw, 1988), pp. 1307–1310.

[18] M. L. W. Thewalt, S. P. Watkins, U. O. Ziemelis, E. C. Lightowlers, and M. O. Henry, Solid State Commun. **44**, 573 (1982).

[19] E. C. Lightowlers, L. T. Canham, G. Davies, M. L. W. Thewalt, and S. P. Watkins, Phys. Rev. B **29**, 4517 (1984).

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

[21] W. M. Chen and B. Monemar, Phys. Rev. B **36**, 7948 (1987).

[22] M.-E. Pistol and B. Monemar, Phys. Rev. B **33**, 7006 (1986).

[23] L. W. Molenkamp and D. A. Wiersma, Phys. Rev. B **32**, 8108 (1985).

[24] W. M. Chen, M. Godlewski, B. Monemar, and P. Bergman (unpublished).

[25] W. M. Chen, M. Donckers, and J. Schmidt (private communication).