Isoelectronic bound excitons in In- and Tl-doped Si: A novel semiconductor defect

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We present the results of detailed transient photoluminescence measurements on the isoelectronic bound excitons associated with the deep acceptors In and Tl in Si. The novel results are explained in terms of a model in which the binding centers can exist in more than one configuration, and in which the bound excitons can make transitions from one configuration to the other. Although the nature of the binding center and the exciton states is not yet known, the transient results are well described by rate equations based upon this model. Additional support is provided by a study of the effects of excitation pulse length on the Si:In transient results, as well as by comparing above-gap excitation versus resonant excitation of the bound excitons.

I. INTRODUCTION

The properties of conventional acceptor- and donor-bound excitons have been studied in great detail in Si by means of photoluminescence spectroscopy.[1] More recently several new luminescence systems observed in Si,[2–21] characterized by very long decay times and high radiative efficiencies, have been attributed to the recombination of isoelectronic bound excitons (IBE). Many of these centers[2–8] show the level structure typical of extended isoelectronic defects (i.e., complexes) with axial symmetry, previously observed in other materials, e.g., GaP:(Cd-O),[22] GaP:(Li-Li-O).[23] In such systems, *j-j* coupling between the electron and hole leads to readily identifiable spectral, transient, and thermalization properties. Certain other luminescence systems, in particular those observed in Si:Cu, Si:In, and Si:Tl (Refs. 9–21) do not manifest any evidence of the usual *j-j* coupling behavior. Of these anomalous isoelectroniclike centers, perhaps the most interesting are those responsible for the *P,Q,R* lines observed in Si doped with the very deep group-III acceptors In and Tl.[9–19] These centers show novel transient and spectral effects which have not been observed for previous isoelectronic defects. Although extremely high luminescence intensities are observed in certain samples, the binding center concentration is so low that absorption measurements have not been possible to date, confirming the extremely high radiative efficiencies of these centers.

The exact nature of the binding center constituents in the Si:Tl and Si:In systems remains an area of controversy. Nearest-neighbor P (Ref. 16) or interstitial Fe (Ref. 24) have both been advanced as the remaining constituents. Work by Ziemelis and Parsons[25] on donor-acceptor pair recombination in Si:(In,P) rules out the possibility that a nearest-neighbor P-In pair is responsible. In addition, we have observed no enhancement of the intensities of these lines after diffusion of Fe into many of our samples.

The *P,Q,R,...* lines were first observed in Si:In by Vouk and Lightowlers,[26] and their isoelectronic nature was later discovered by Mitchard *et al.*,[9] who erroneously concluded, however, that the three main lines arose from three different binding centers. The independent discovery by Thewalt *et al.*[11] and Weber *et al.*[12] that the intensity of these spectral lines could be greatly enhanced by rapidly quenching the samples from 1300 K to room temperature, made possible a detailed study of their transient and spectral properties. The Si:In photoluminescence[13] and excitation[17,18] spectra have been described in detail elsewhere, along with possible level schemes for the initial and final states. Application of the same quenching treatment to samples of Si doped with the even deeper acceptor Tl was found to produce a completely new set of photoluminescence lines.[15] At ~20 K these lines had a remarkable similarity to the *P,Q,R* system in Si:In, but with the principal no-phonon transition displaced to lower energy by 67.4 meV relative to the Si:In *P* line (see Fig. 1). This energy difference was noted to correspond to a large fraction of the 91-meV difference between the Tl and In acceptor binding energies, indicating that the central cell potential of the acceptor was important in binding excitons to these defects. The long lifetimes of the Tl-related luminescence lines (~25 μs) were again indicative of an isoelectronic binding center. In view of the close similarities to the Si:In system, the three principal lines were also denoted *P,Q,R*.

Whereas the Si:In *P,Q,R,...* luminescence spectra do not change significantly over the 1.6- to 25-K range, the Si:Tl *P,Q,R,...* luminescence vanishes completely below 12 K and is replaced by a new set of lines denoted *A,B,C,...* for which the ground state to ground state transition (*A* line) lies 36.8 meV above the Si:Tl *P* line.[13] The temperature dependence of this novel changeover is shown in Fig. 2. The long lifetimes (~50 μs) of these new lines are also suggestive of IBE recombination. The spectral characteristics and possible level structure of this luminescence system has been described in detail previously.[13]

The observation that the integrated luminescence intensity of all Si:Tl lines does not change appreciably in passing through the changeover temperature, and that no sample dependence of the relative line intensities is observed, suggested that the two luminescence systems (*P,Q,R,...* and *A,B,C,...*) are due to the recombination of excitons

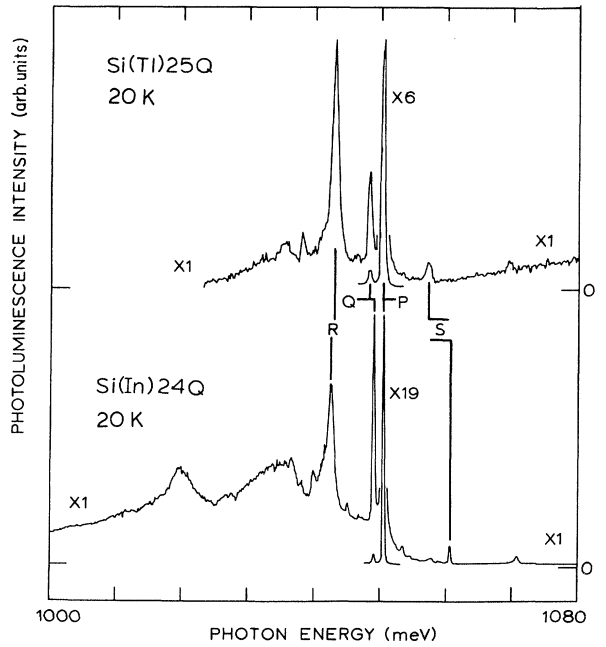

FIG. 1. Photoluminescence spectra of the Si:Tl and Si:In isoelectronic centers recorded at 20 K. The Si:In spectrum has been shifted down in energy by 67.4 meV in order to align the principal no-phonon P lines and thus emphasize the similarities in the spectral features.

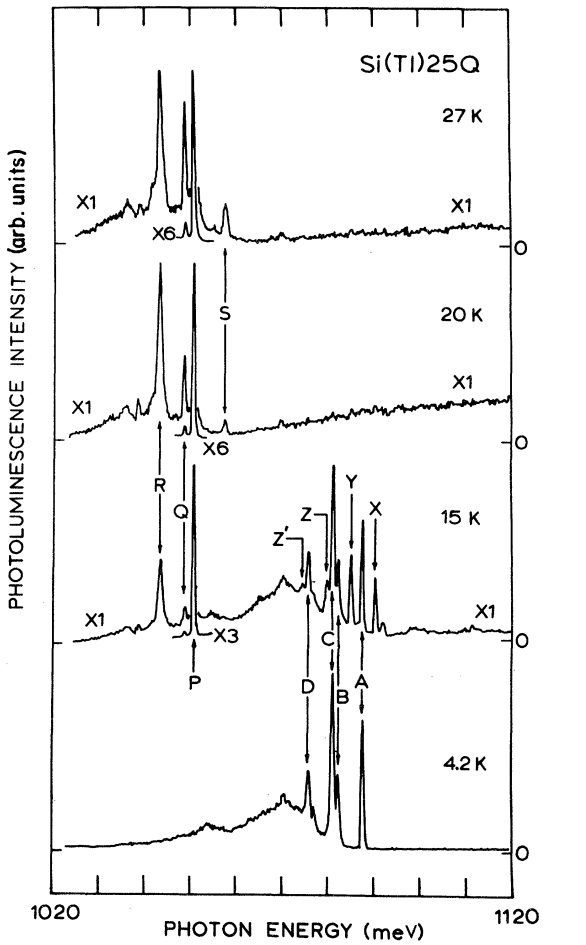

FIG. 2. Photoluminescence spectra of the Si:Tl isoelectronic center recorded at various temperatures, showing the changeover in spectral features. The details of the spectra are more thoroughly examined in Ref. 13.

at the same binding center.[13] The transient photoluminescence results which follow clearly show that this is the case. These data indicate that for Si:Tl, excitons are initially captured into a configuration of the defect responsible for the $A,B,C,\ldots$ lines, but once captured can undergo a thermally activated changeover into a different IBE configuration responsible for the $P,Q,R,\ldots$ lines. For brevity the two configurations are referred to as A-type centers or P-type centers, respectively.

In a previous paper[19] new transient photoluminescence data were presented for the Si:In IBE, which also suggested a configurational changeover for this system. The transient data, while substantially different from those of Si:Tl, nevertheless were explained by invoking two different exciton configurations A and P, by analogy to the Si:Tl case, but in which A-center radiative transitions are not observed. Another difference is that for the Si:In case both A- and P-type IBE are formed during the initial capture of free excitons (FE).

A general model for describing the Si:In and Si:Tl IBE behavior is shown in Fig. 3. This is the model we have previously proposed[19] to explain our preliminary Si:In and Si:Tl results and will be used here to set up the rate equations with which we will obtain fits to the experimental data. In this model it is assumed that the binding center, which is known to consist of two or more constituents, can exist in two different configurations. Furthermore, it must be assumed that the energy differences between the two configurations can be significantly changed, and in the Tl case, reversed when an exciton binds to the bare center. Referring to Fig. 3, which is appropriate for Si:Tl, we see that the energy difference between the A and P lines must equal $\Delta E_1 - \Delta E_2$. The figure also defines some of the reconfiguration times which will be used in the rate equations in later sections.

The Si:Tl results can be qualitatively explained as follows. At all temperatures of interest, kT is less than ΔE_1, so the bare binding centers are in the A configuration, and upon capturing FE produce A-type IBE. At low temperatures, the A state radiative lifetime τ_A is short compared to τ_{AP}, presumably because of a large energy barrier to reconfiguration, and only A luminescence is observed. As T increases, τ_{AP} decreases due to thermally activated crossing of the barrier, and some A-type IBE are converted to P-type IBE, resulting in $P,Q,R,\ldots$ luminescence. At high T, τ_{AP} becomes much shorter than τ_A, so the A-type luminescence vanishes and is replaced completely by P-type luminescence. This fact, within the framework of the model, places the P exciton energy below that of the A exciton, as shown in Fig. 3.

The model of Fig. 3 can also explain the Si:In data, if ΔE_1 and ΔE_2 are taken to be small and τ_A is very long. Since ΔE_1 is small, at nonzero T both configurations of

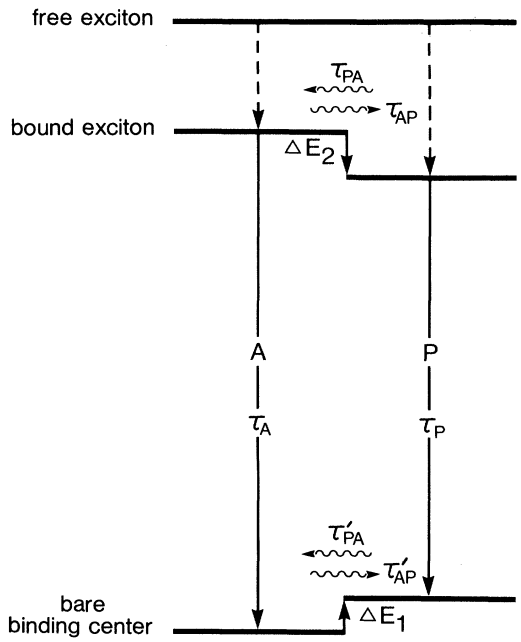

FIG. 3. Simple energy level model to describe the Si:Tl and Si:In transient results. See text for a description of the relevant parameters.

the bare binding center are present, and both A- and P-type IBE are therefore formed upon FE capture. The initial A/P population ratio would be expected to be thermally activated with an activation energy ΔE_1, which is shown to be the case. It is possible that during the FE capture process, which presumably cascades through various IBE excited states, reconfiguration may occur. This clearly does not take place in Si:Tl below 10 K, but we shall later demonstrate that for Si:In the different states of the P-type IBE have significantly different probabilities of reconfiguring into A-type IBE. In our Si:In model $\tau_A > \tau_{AP} > \tau_P$, and reconfiguration into P-type IBE appears to be the major decay mechanism for the A-type IBE, as evidenced by the fact that no A-type luminescence is ordinarily observed in Si:In. At low T, τ_{AP} reaches a tunneling limit, which is independent of T, and at higher T, τ_{PA} decreases rapidly due to thermal activation. Evidence will be provided which shows that above 10 K, τ_{PA} also becomes short compared to τ_P, implying that ΔE_2 is also small for Si:In.

It is important to note that the assumption that there exist two distinguishable metastable bare center configurations is not strictly required to fit the data presented here. Suppose that the upper bare center energy level was not metastable, but relaxed back to the lower level in a time short compared to the radiative time constants involved here. If this were the case then the relative initial IBE populations in Si:In would be determined, not by the equilibrium concentration of bare A and P centers but by some branching process which occurred during exciton capture. For definiteness, however, we will continue to assume two metastable bare center configurations in the model expressed by Fig. 3.

Previously, a model for the Si:Tl results had been put forth in which the temperature-induced $A \rightarrow P$ changeover was due to the removal of some mobile particle from the binding center as T was increased.[13] The main argument for this view was that the very rapid change in the spectral properties over a few K implied a large preexponential factor consistent with a bound-to-free transition. This model was abandoned[19] once it became clear that this large preexponential factor was most likely associated with the high attempt frequency characteristic of phonon-mediated processes, such as the reconfiguration of the binding center in the presence of an energy barrier.

In the following sections we will demonstrate that the details of the transient response of these systems versus temperature can be well described in terms of the model of Fig. 3. The agreement of both the lifetime and intensity ratio results supports the validity of the model. Further support is provided by additional experiments in Si:In. In one such test the intensity ratio of the two components of the photoluminescence at a fixed temperature was shown to vary with excitation pulse length in a manner which is in qualitative agreement with the model. Also, transient experiments using resonant excitation of Si:In IBE into their ground or excited states reveal the expected results.

II. EXPERIMENTAL

The measurements undertaken in this study were obtained using a variety of samples obtained from various sources. Of the Si:In samples which gave the highest signal levels, one was cut from a boule of Czochralski-grown Si:In with a nominal concentration of 4×10^{15} In per cm^{-3} (Si:In 24), and the other from a boule of float-zone-refined material with a concentration of approximately 2×10^{16} In per cm^{-3} (Si:In 112). For the Si:Tl measurements two samples were available, one with a concentration of 5×10^{16} Tl per cm^{-3} (Si:Tl 21) and the other with a much lower doping level of 4×10^{14} Tl per cm^{-3} (Si:Tl 25). The latter samples offered substantially cleaner spectral and transient curves due to the absence of spectral inteferences and broadenings caused by the high level of Sn impurities in Si:Tl 21. All samples were subjected to the same quenching procedure, which consisted of briefly heating to ~900°C—1100°C and dropping the samples into a 50 vol%:50 vol% ethanol:H_2O mixture, followed by etching in HNO_3:HF.

The samples were cooled to 1.4—4.2 K by pumping on the sample chamber of a He immersion Dewar. Temperatures above 4.2 K were obtained using a variable temperature Dewar, in which the samples were pressed into an In pad soldered to a Cu heater block, which was cooled by contact with cold He gas. The block temperature was measured with a calibrated Si diode sensor and electronically regulated.

Sample excitation was provided by several different light sources. For above-band-gap excitation, Ar^+- and Kr^+-ion lasers provided several lines in the region from 514.5 to 799.3 nm. The output of these lasers could be modulated to achieve pulse widths of 10 μs and up by means of a mechanical chopper wheel, or by using the

acousto-optic modulator in a Harris mode locker head to turn the laser on and off by driving it at a radio frequency different from the mode-locking frequency. The latter technique resulted in very rectangular pulses of adjustable length, having turn-on and turn-off times of about 2 μs. In applications where very short excitation pulses were required, a liquid-nitrogen-cooled GaAs laser diode array provided pulses of $\sim$100 ns width at 870 nm with rise and fall times of about 10 ns.

In addition to these above-band-gap spectral sources, resonant excitation of the Si:In samples was obtained by means of a pulsed dye laser pumped optical parametric oscillator (Chromatix CMX4 IR), using Rhodamine-640 dye. This device provided near-infrared pulses of a few tenths of an mJ energy, with widths of less than 1 μs, tunable over the 1.0—1.2 μm resonant absorption region of the Si:In centers. A GaAs light emitting diode provided output in the vicinity of 940 nm for applications which required low-level, above-band-gap excitation of the Si:In samples.

The photoluminescence signal was analyzed by means of a $\frac{3}{4}$-m double spectrometer with 600 lines/mm gratings, blazed for 1 μm. For most transient data, the signal was processed in the photon counting mode using an enhanced infrared response GaInAsP photomuliplier tube (Varian Associates VPM159A3), in conjunction with a computer-controlled multichannel scaler (MCS). In addition, a liquid-nitrogen-cooled intrinsic Ge detector (Northcoast E0817) was used for spectra measurement at wavelengths up to 1.7 μm. This detector does not suffer the sharp dropoff in quantum efficiency at 1.2 μm inherent in the photomultiplier detector.

III. Si:Tl TRANSIENT RESULTS

While some preliminary Si:Tl transient measurements were reported previously,[11,13] this paper gives the first detailed analysis and interpretation of the transient behavior over a range of temperatures. The measurements reported here were obtained with the lightly doped Si:Tl 25 sample, using the pulsed GaAs laser diode excitation source. Similar results have also been obtained with the Si:Tl 21 sample.

The decay curves of all $A,B,C,\ldots$ related lines were identical at any given temperature, confirming that all lines arise from a single isoelectronic binding center. Below 10 K, all lines decayed with a single exponential time constant of $\tau_A = 53$ μs, which is taken as the radiative time constant for the A centers. Figure 4 shows representative decay spectra for the 7—16 K temperature range, in which the spectral changeover occurs. The observed A-type IBE lifetime, τ'_A is observed to reach a very short value above 16 K, at which temperatures the integrated A-center luminescence intensity also goes to zero (Fig. 2). The data presented in Fig. 4 share the same baseline, so the close agreement of the intensities immediately after the excitation pulse indicates that the initial concentration of A-centers is essentially independent of temperature.

The $P,Q,R,\ldots$ transient data show a markedly different behavior, as indicated in Fig. 5. At intermediate A

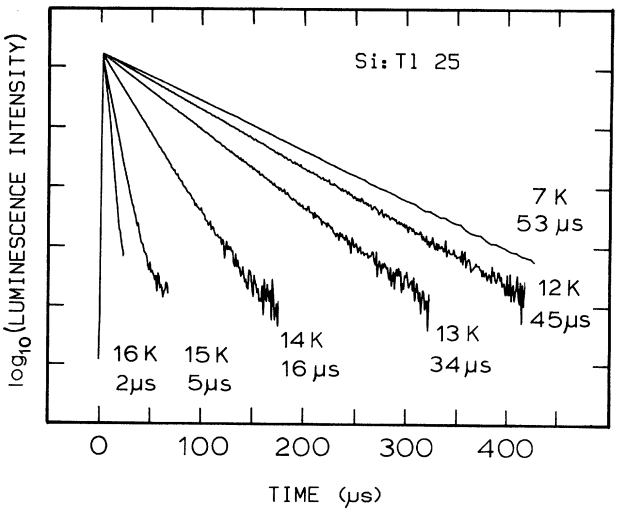

FIG. 4. Representative transient curves from the Si:Tl $A,B,C,\ldots$ lines over the temperature range in which the spectral changeover occurs. At 7 K and below, $\tau'_A = 53$ μs. Above 16 K, $\tau'_A < 1$ μs. Vertical axis markers are decades.

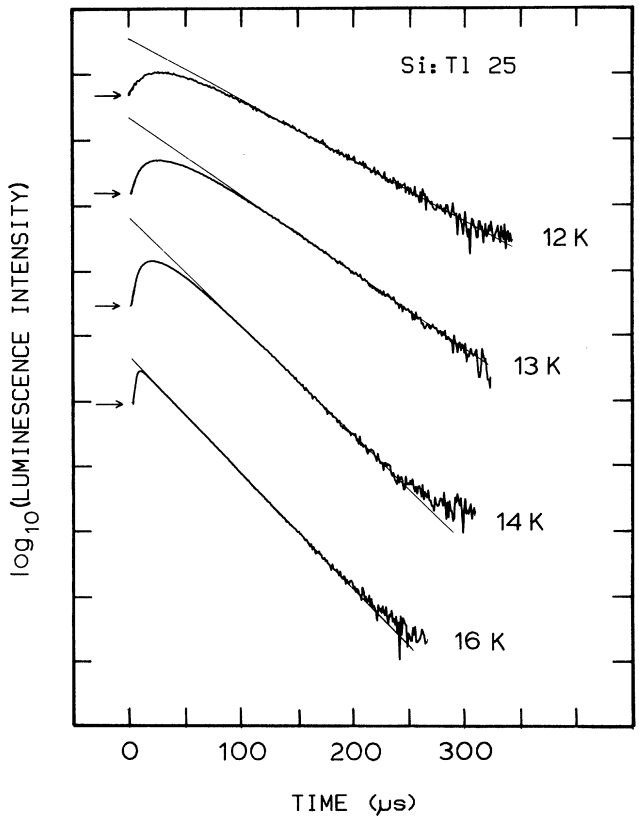

FIG. 5. Representative Si:Tl $P,Q,R,\ldots$ line transient curves over the same temperature range as Fig. 4. Straight lines are least-squares fits to the long-time portion of the curves. Vertical axis markers are decades. The four curves have been displaced horizontally for clarity. In each, the intensity rises to the point marked by the arrow within the instrumental resolution, and then rises more slowly before decaying.

to P changeover temperatures (12–16 K), a relatively slow buildup of the luminescence intensity is observed immediately after the laser pulse, followed by subsequent simple exponential decay. In this temperature range, the $P,Q,R,\ldots$ transient response could always be fitted, within experimental error, to a sum of two exponentials of the form

$$I = I_0(e^{-t/\tau_L} - e^{-t/\tau_S}) , \tag{1}$$

where τ_L is the decay time of the exponential, long-time portion of the curve, and τ_S is the buildup time constant ($\tau_S < \tau_L$). The experimentally obtained values of these time constants are shown in Fig. 6 where they are compared with the A-center decay times. The τ_S values were obtained by subtracting the experimental P-center decay points shown in Fig. 5 from least-squares fits to the long-time decay portion of those curves. The resulting curves were exponential over at least two decades.

At temperatures above 18 K, the P-line buildup is so rapid that it cannot be resolved, and the MCS output shows a single exponential decay with a time constant of $\tau_L = 25$ μs, which is interpreted as the radiative lifetime of the P centers, τ_P. Below 12 K the P-center luminescence intensity was so weak that transient measurements became impossible. The above results were independent of the repetition rate, excitation intensity, and of the particular sample used.

The transient data of Fig. 6 are accurately described within the preceding model by the following simple rate equations:

$$\frac{dn_A}{dt} = -\frac{n_A}{\tau_A} - \frac{n_A}{\tau_{AP}} , \tag{2}$$

$$\frac{dn_P}{dt} = -\frac{n_p}{\tau_P} + \frac{n_A}{\tau_{AP}} , \tag{3}$$

where n_A and n_P are the A-type and P-type IBE populations, τ_A and τ_P are their respective radiative decay times, and τ_{AP} is the time constant for changeover from an A center to a P center. In principle there may also be transitions from P centers to A centers, but the energetics of the Si:Tl case appear to preclude this.

Assuming initial exciton populations $n_A(0) = N_A$ and $n_P(0) \sim 0$ gives

$$n_A(t) = N_A e^{-t/\tau_{A'}} , \tag{4}$$

$$n_P(t) = \frac{\tau_p}{\tau_{AP}} \left[\frac{\tau'_A}{\tau'_A - \tau_P} \right] N_A (e^{-t/\tau_{A'}} - e^{-t/\tau_P}) , \tag{5}$$

where $1/\tau'_A = 1/\tau_A + 1/\tau_{AP}$ is the total A-center decay rate, which is what we observe experimentally. Thus measurement of the temperature dependence of $1/\tau'_A$, in conjunction with the observed radiative A-center decay time of $\tau_A = 53$ μs gives the temperature dependence of τ_{AP} which is plotted in Fig. 7. A least-squares fit to this data yields an exponential activation of the changeover time constant given by

$$\tau_{AP} = \tau_0 e^{+E_B/kT} , \tag{6}$$

where $\tau_0 = 1 \times 10^{-12}$ s and $E_B = 20.5$ meV. E_B is interpreted as the energy barrier to reconfiguration of the A centers into P centers.

The predictions of Eq. (5) using the stated parameters, are shown in the solid line in Fig. 6, superimposed over the experimental data points. The crossover point of the two lines occurs at 13.5 K where $\tau_L = \tau_S$, or equivalently, $\tau'_A = \tau_P$. The horizontal line to the left of the intersection represents the prediction $\tau_S = 25$ μs $= \tau_P$ for $T \leq 13.5$ K, while the horizontal line to the right of the intersection represents the prediction that $\tau_L = 25$ μs for $T \geq 13.5$ K. The line rising from the crossover point gives the predicted values for τ'_A and τ_L at $T \leq 13.5$ K, while the line below the intersection is for τ'_A and τ_S at $T \geq 13.5$ K. The agreement is seen to be excellent.

From the absence of $P,Q,R,\ldots$ luminescence below 10 K one can obtain a lower limit on the low-temperature value of the changeover time constant τ_{AP}. At low T, P center luminescence would probably be undetectable if its integrated intensity were less than 10^{-2} times that of the

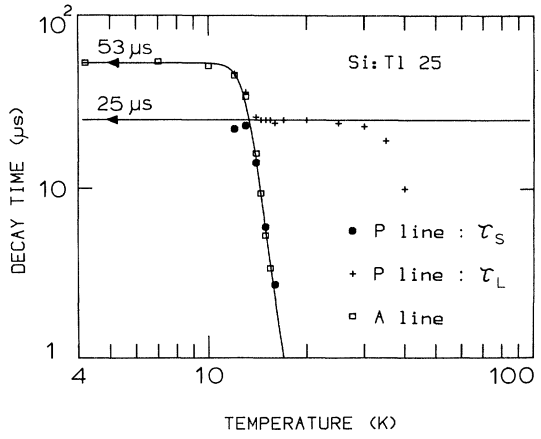

FIG. 6. Summary of Si:Tl transient data as a function of temperature. Open squares represent $A,B,C,\ldots$ luminescence decay times. τ_S and τ_L refer to the buildup time and long-time decay constant of the $P,Q,R,\ldots$ luminescence, respectively. Solid lines are fits using the rate equation analysis given in the text. The drop in τ_L for the P line above 30 K is due to thermal dissociation.

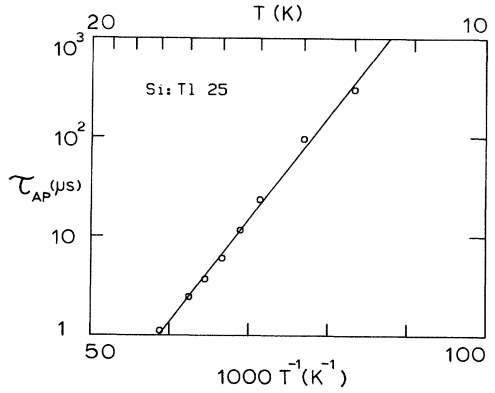

FIG. 7. Log of the A to P center changeover time constant τ_{AP} as a function of $1/T$. A least-squares fit to the data gives an activation energy of 20.5 meV and a prefactor of $\tau_0 = 10^{-12}$ s.

A-center luminescence, given the fact that the broad phonon structure of the $A,B,C,\ldots$ lines interferes with the $P,Q,R,\ldots$ lines below ~ 12 K. This gives a lower limit of $\tau_{AP} \geq 10^2 \tau_A = 5$ ms.

IV. Si:In TRANSIENT RESULTS

In contrast to the Si:Tl data, the Si:In isoelectronic system shows no evidence of a significant change in spectral features between 1.4 and 30 K. Until recently it had also been assumed that the decay of the $P,Q,R,\ldots$ luminescence in Si:In was governed by a single exponential, with little temperature variation over the range 1.4—20 K (Refs. 9 and 13) (above 20 K thermal dissociation begins to increase the decay rate). With the huge enhancements in intensity obtained with the thermal quenching procedure, coupled with better data acquisition techniques, it has recently been shown that the temperature dependence of the Si:In transient data is more complicated.[19]

Figure 8 gives a summary of the behavior of the Si:In decay curves over the temperature interval in which the data change significantly. These preliminary data were obtained with above-band-gap, pulsed excitation from the GaAs laser diode array. The curves are characterized by two well-defined exponential decay constants τ_S and τ_L at temperatures up to 10 K, beyond which temperature all lines decay with a single time constant of 230 μs. At all temperatures the decay curves can be fit to within experimental error by an expression of the form

$$I = I_{S0} e^{-t/\tau_S} + I_{L0} e^{-t/\tau_L} . \tag{7}$$

At 1.4 K, τ_S and τ_L limit at 163 and 3400 μs, respectively. As the temperature is increased, both time constants become shorter, while the ratio of the exponential prefactors I_{S0}/I_{L0} decreases, until at 10 K, $I_{S0} \sim 0$ and the system decays with a single time constant, $\tau_L = 230$ μs. The measured temperature variation in τ_L and τ_S is summarized in Fig. 9. The values of τ_S were obtained by subtracting least-squares fits to the long-time portion of the decay curves from the raw data. In all cases, the resulting curves were exponential over at least two decades. Figure 10 gives a plot of the measured temperature variation of the initial intensity ratio, I_{S0}/I_{L0}. Earlier studies in which only the first two decades of decay were observed missing the long-time component, which is present below 10 K, and therefore reported only a small variation in the exciton decay constant over this temperature range.[9,13]

The Si:In decay data were sample independent, based on measurements on samples cut from boules of differing origin and In concentration. No dependence on sample preparation, i.e., quenching rate, duration of heating cycle, or initial temperature, was observed. Similar features were observed in all the phonon replicas, ruling out the possibility of spurious spectral interferences.

These transient data can be accounted for in detail within the framework of the general energy level model (see Fig. 3) previously applied to Si:Tl. In the case of Si:In, it is assumed that the $P,Q,R,\ldots$ system arises from IBE recombination at P centers, and that the radiative lifetime of the A centers, τ_A, is much longer than the A to P reconfiguration time, τ_{AP}. The long-time decay portion of the transient $P,Q,R,\ldots$ luminescence results from tunneling of initially created A centers into P centers. At temperatures below 4.2 K, τ_S maintains the roughly constant value of 163 μs, which is taken as the P-type IBE radiative lietime, τ_P. In this temperature regime the ratio of the initial populations is just given by the ratio of the integrated intensities of the two exponentials. The long-time constant τ_L decreases somewhat as the temperature is increased from 1.4 to 4.2 K. This is interpreted as arising from a thermally activated increase in the A- to P-center tunneling rate. As the temperature is increased in this regime the ratio of I_{S0}/I_{L0} decreases so as to hold the

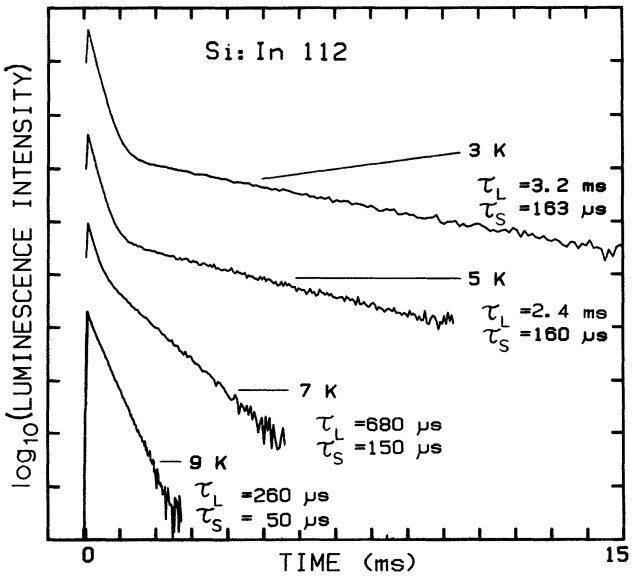

FIG. 8. Representative Si:In transient curves showing the double exponential decay behavior below 10 K. Above 10 K all data decay with a single 230-μs time constant. Vertical axis markers are decades.

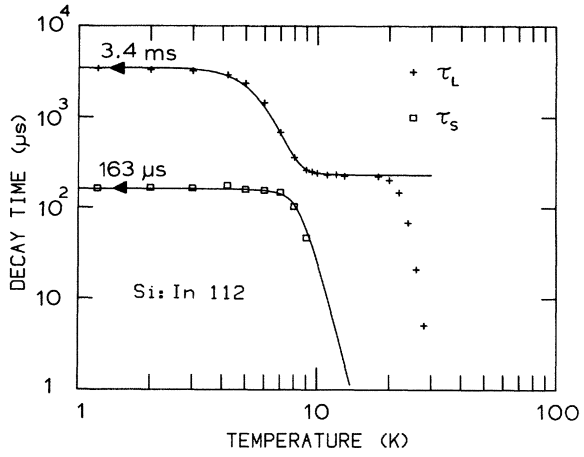

FIG. 9. Summary of Si:In transient data. τ_S and τ_L refer to the short- and long-time constant components of the luminescence decay, respectively. Solid lines are best fits using the rate equation analysis outlined in the text. The drop in τ_L above 20 K is due to thermal dissociation.

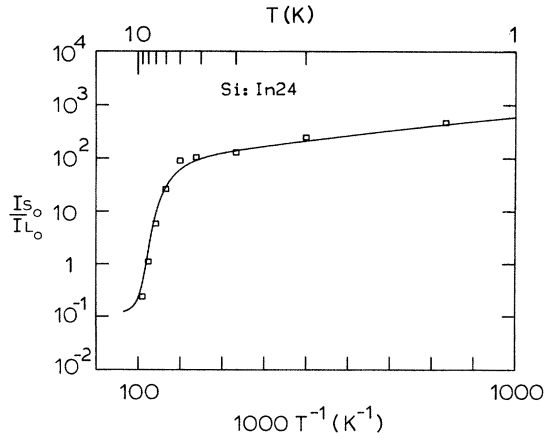

FIG. 10. Ratios of the initial intensities of the two photoluminescence decay components, I_{S0}/I_{L0}, for Si:In as a function of temperature. The solid line is a theoretical fit using the same parameters used in Fig. 9.

integrated intensities of each exponential roughly constant. Actually, there is a small change in the ratio of these integrated intensities between 1.4 and 4.2 K. The data presented in Fig. 10 imply a small 0.2-meV activation of the initial bare binding center concentration ratio, $n_P(0)/n_A(0)$. Within the model of Fig. 3, this implies that $\Delta E_1 = -0.2$ meV, with the bare A-center energy lying just above that of the bare P center (assuming that reconfiguration during exciton capture is negligible). Alternatively we could assume that only one species of binding center is present, but both types of IBE are formed during capture, with a temperature-dependent branching ratio. Since this does not take place for Si:Tl, the first possibility seems more likely.

A further increase in temperature above 4.2 K results in a rapid decrease in τ_L due to thermal activation of τ_{AP}. The concurrent rapid decrease in τ_S is ascribed to the onset of the reverse process of reconfiguration of P centers into A centers, governed by a thermally activated reverse changeover rate, τ_{PA}. At temperatures of 9 K and above, the feedthrough time constants τ_{AP} and τ_{PA} become small compared to the radiative P-center decay time τ_P. In this regime both centers decay with a single exponential $\tau_L = 230$ μs. This value is greater than $\tau_P = 163$ μs, since the excitons now spend more time in the long-lived A configuration. This gives a constraint on the effective degeneracy ratios g_A and g_P, since if we assume $\tau_A = \infty$ the high-temperature decay time is given by

$$\tau_L = \tau_P(g_A + g_P)/g_P \ . \tag{8}$$

Given $\tau_L = 230$ μs, $\tau_P = 163$ μs this implies $g_P/g_A = 2.4$.

The above model can be presented in a more quantitative manner by means of the following rate equations:

$$\frac{dn_A}{dt} = -\frac{n_A}{\tau_A} - \frac{n_A}{\tau_{AP}} + \frac{n_P}{\tau_{PA}} \ , \tag{9a}$$

$$\frac{dn_P}{dt} = -\frac{n_P}{\tau_P} + \frac{n_A}{\tau_{AP}} - \frac{n_P}{\tau_{PA}} \ , \tag{9b}$$

which are a generalization of the Si:Tl equations, with the addition of the reverse feedthrough channel, n_p/τ_{PA}. The solutions of these equations are of the form

$$n_A = Ae^{-t/\tau_L} + Be^{-t/\tau_S} \ ,$$
$$n_P = Ce^{-t/\tau_L} + De^{-t/\tau_S} \ , \tag{10}$$

where τ_L, τ_S, and the prefactors are given by simple analytic expressions determined by the various time constants and by the initial populations, $n_A(0), n_P(0)$. Unfortunately the only directly observable time constant in Eqs. (9) is τ_P. However, for lower T we can also observe the total decay constant for the A-type IBE, $\tau'_A = (1/\tau_A + 1/\tau_{AP})^{-1}$, which is simply the measured τ_L of the decay curves. Since τ_A appears to be very large, the approximation $\tau'_A \sim \tau_{AP}$ is likely valid.

In addition, the feedthrough time constant τ_{AP} cannot have the simple classically activated form obtained for Si:Tl, since there appears to be a zero-point tunneling contribution to the feedthrough at low temperatures, which results in a long decay component even at 1.4 K. This does not imply a substantial difference in the changeover processes between Si:In and Si:Tl, since for the latter case we were only able to set a lower limit of $\tau_{AP} \geq 5$ ms at low T. Thus the Si:Tl center might also have some unobserved A to P tunneling.

The saturation of the Si:In long-time component, $\tau_L = 3400$ μs at 1.4 K, places a constraint on this tunneling limit of τ_{AP}. A general expression for τ_{AP}, which allows for a zero-point tunneling limit at low T, as well as the classically activated form of Eq. (6) at high T, is given by

$$\tau_{AP} = \tau_0 e^{+E_B/kT^*} \tag{11}$$

where

$$kT^* = \frac{\hbar\omega}{2}\coth\left[\frac{\hbar\omega}{2kT}\right] .$$

This expression represents the time constant for nonradiative transitions between two electronic levels separated by an energy barrier E_B, and coupled to the same phonon mode, of energy $\hbar\omega$. Such expressions are well known for theories of nonradiative transitions in large molecules[27] and nonradiative capture at deep impurities in semiconductors.[28] The following limits are implied:

$$\tau_{AP} = \tau_0 e^{+2E_B/\hbar\omega}, \quad kT \ll \hbar\omega \tag{12a}$$

$$\tau_{AP} = \tau_0 e^{+E_B/kT}, \quad kT \gg \hbar\omega \ . \tag{12b}$$

In the low-temperature limit, the observed value of $\tau_{AP} = 3400$ μs provides a constraint on τ_0, E_B, and $\hbar\omega$ via Eq. (11). Thus only two of these quantities need be used as independent fitting parameters.

The reverse feedthrough time τ_{PA} must have a form similar to that of τ_{AP}, under the previously stated assumption of $\Delta E_2 \sim 0$. The ratio of the degeneracy factors g_A/g_P given in (8) implies that, above 10 K $\tau_{PA} = (g_P/g_A)\tau_{AP} = 2.4\tau_{AP}$. We therefore assume

$$\tau_{PA} = 2.4\tau_0 e^{+E_B/kT^*} \tag{13}$$

over the entire temperature range of interest (1.4–20 K). If we were to allow for a small positive ΔE_2, then τ_{PA} would go to infinity at sufficiently low temperature, but this would not change our results.

We are now in a position to fit the lifetime data presented in Fig. 9 by solving the rate equations (9) for τ_L and τ_S. The only adjustable parameters will be τ_0, E_B, and $\hbar\omega$. Very close agreement with the experimental data is shown by the solid line in Fig. 9 which assumes the fitting parameters: $\tau_0 = 10^{-13}$ s, $E_B \sim 20$ meV, $\hbar\omega \sim 1$ meV. These are close to the experimentally observed values in Si:Tl, i.e., $\tau_0 = 10^{-12\pm1}$ s, $E_B = 20.5$ meV.

As a check on the validity of this fit, these parameters should also give a good fit to the experimental I_{S0}/I_{L0} values given in Fig. 10. The 0.2-meV activation of I_{S0}/I_{L0} evident in Fig. 10 at low T is explicitly entered into the solution of the rate equations by assuming that the initial population ratio is thermally activated, i.e., $n_P(0)/n_A(0) \propto e^{+(0.2\text{ meV})/kT}$. The solid line in Fig. 10 shows very good agreement in the temperature interval from 4.2 to 10 K, in addition to the expected agreement at low temperatures. The closeness of fit in Figs. 9 and 10 can be taken as confirmation of the general validity of the overall energy level model.

V. LONG EXCITATION PULSE EXPERIMENTS IN Si:In

Another test of our model for the Si:In transient results involves a study of the decay curves versus the duration of excitation at some fixed temperature. As we have already stated, the transient curves are dependent *only* on sample temperature under the usual conditions of short (much less than τ_S or τ_L) excitation pulses. However, if we use long excitation pulses (on the order of τ_S or longer) we would expect I_{S0}/I_{L0} to decrease, since under the assumption of a constant ratio of generation rates into A-type and P-type IBE, one would expect a larger population buildup in the longer-lived A configuration. At 4.2 K $I_{S0}/I_{L0} = 104$ for short excitation pulses, and using $\tau_S = 163$ μs and $\tau_L = 2700$ μs, we find that the initial P-type IBE to A-type IBE concentration ratio, and thus the generation rate ratio, is 6.1 (under the previously stated assumption that $\tau'_A = \tau_{AP}$). If this same generation rate ratio applies to long excitation pulses, then the transition rate ratio in the limit of long excitation pulses should be 6.1 to 1 (P type to A type) in the simplest model where all A-type IBE reconfigure into P-type IBE. Thus, immediately after a long excitation pulse, one would expect a double exponential decay with the same τ_L and τ_S but with a greatly reduced $I_{S0}/I_{L0} = 6.1$ (at 4.2 K).

Initial attempts to observe this effect with chopped 514.5-nm excitation from an Ar-ion laser operated at relatively high excitation power were unsuccessful—I_{S0}/I_{L0} remained near 100 independent of excitation pulse length. After some reflection, we postulated that this negative result could be due to our operation in the high excitation denity limit, due to the very small sample volume excited by the 514.5-nm radiation and the very low density of binding centers (less than 10^{14} cm^{-3}, as determined by the absence of observable absorption). In the model represented by Fig. 3, the ratio of the generation rates of the two types of IBE could be altered during long pulses at high FE densities, if after IBE recombination the bare binding centers captured new FE in a time short compared to the time taken for the two configurations of the bare binding center to equilibrate.

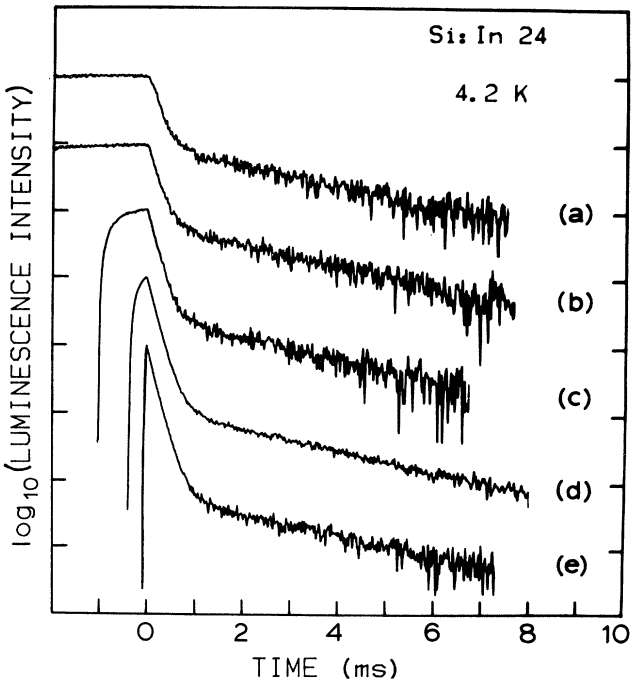

FIG. 11. Transient spectra obtained with very low level light emitting diode excitation, showing the dependence of I_{S0}/I_{L0} as a function of excitation pulse widths of (a) 20 ms, (b) 4 ms, (c) 1 ms, (d) 425 μs, and (e) 100 μs.

To test this hypothesis, long pulse transient experiments were performed at much lower excitation densities using the ~940-nm output of a GaAs light emitting diode to provide a much larger excitation volume. Excitation intensities at the sample surface were varied between 10 and 500 μW/cm^2. By using this source, a strong dependence of I_{S0}/I_{L0} on excitation pulse length was observed. Some of the decay curves are shown in Fig. 11, and all of the results are summarized in Fig. 12. The solid curve in Fig.

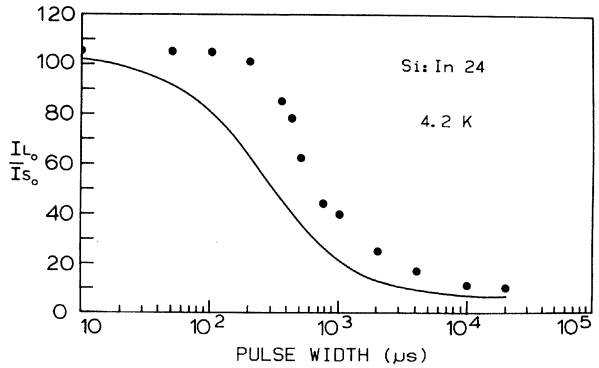

FIG. 12. Points represent experimental I_{S0}/I_{L0} values as a function of excitation pulse width. The solid line represents a theoretical curve based on the model presented in the text.

12 is the theoretical prediction based upon a fixed generation rate ratio of 6.1. The discrepancy between this curve and the data may indicate that we were still not operating in the low excitation density limit, but the value of $I_{S0}/I_{L0} \simeq 9$ at 20 ms pulse length is reasonably close to the predicted result. This value of I_{S0}/I_{L0} could only be obtained when the light emitting diode was operated at very low power levels.

VI. RESONANT EXCITATION OF Si:In IBE

An important test of this model is provided by resonantly creating the IBE, either in their ground or excited states, using a pulsed, tunable excitation source, and then monitoring the luminescence decay curves. Continuous wave excitation spectroscopy of the Si:In IBE has already been carried out using a color-center laser.[17,18] To obtain transient excitation spectra we used the previously described flashlamp dye laser pumped optical parametric oscillator operating at a repetition rate of 20 Hz. The excitation spectra obtained by monitoring the P or R line photoluminescence are shown in Fig. 13 and are very similar to previously published results.[17,18] The lines are labeled according to the scheme of Wagner and Sauer,[18] with P_0^0 being the principal no-phonon P line.

By using resonant excitation we should be able to alter I_{S0}/I_{L0}, since we should in principle be able to produce pure A-type or P-type IBE. By pumping the P line, for example, we would expect to produce pure P-type IBE, so the decay curve should be a single exponential with lifetime equal to τ_P (this neglects a small effect which may arise due to τ_{PA}). Similarly, if any of the observed excited states were due to transitions to A-type IBE, we would expect to observe a single exponential decay with a lifetime of τ_A'. In fact, our results indicate that all of the excitation peaks feed predominantly into P-type IBE.

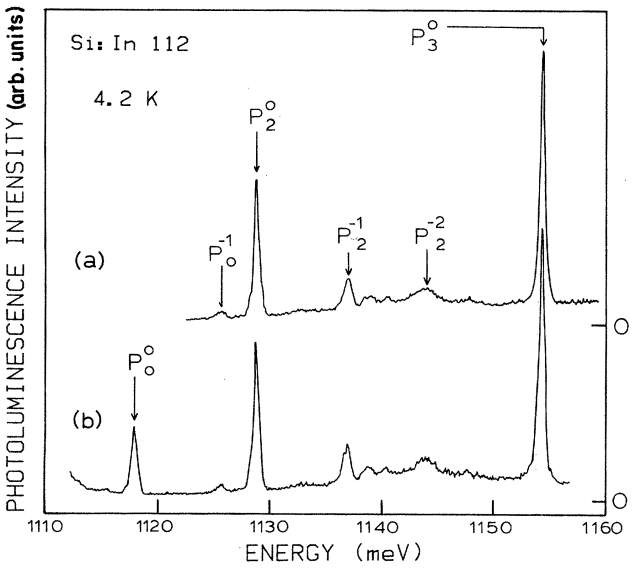

FIG. 13. Excitation spectra obtained with an optical parametric oscillator. Curves (a) and (b) correspond, respectively, to monitoring the photoluminescence intensity at the P line or the R line. The energy given is that of the pump photons.

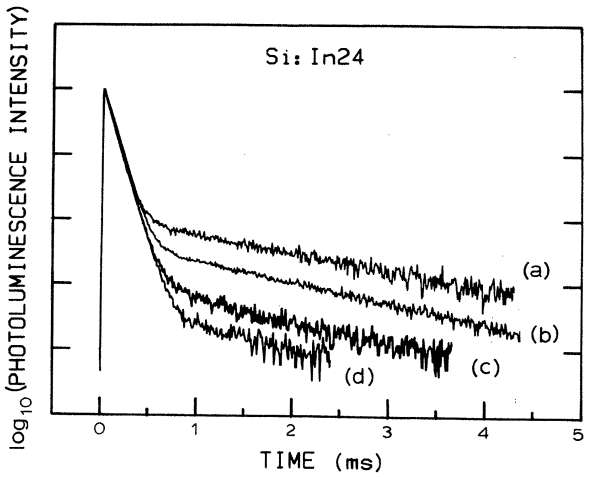

FIG. 14. Representative decay curves obtained using resonant pulsed excitation. The curves represent the result of (a) pumping just above the FE absorption edge at 4.2 K, (b) pumping into P_3^0 at 4.2 K, (c) pumping into P_2^0 at 4.2 K, and (d) pumping into P_2^0 at 1.4 K. Luminescence was monitored at the P_0^0 wavelength. The spectra are aligned so that their initial intensities coincide. Vertical axis markers are decades.

Some of the observed decay curves are shown in Fig. 14, while the results are summarized in Table I. We should emphasize again that the values of τ_S and τ_L depend only on temperature, not the mode of excitation. It is I_{S0}/I_{L0} which depends both upon temperature and the type of excitation. The top entry in Table I is for a pump wavelength of 1.05 μm, which is just above the FE absorption edge in the TA phonon replica. The I_{S0}/I_{L0} ratios for the P-line luminescence are seen to be identical to those obtained for visible excitation sources, as expected. We note also that the ratios for the R line are smaller than for the P line. The reasons for this will become apparent in the next section.

The next two lines in the table give the result for pumping into P_3^0 and P_2^0 while monitoring P. It is clear that both transitions give higher P-type IBE to A-type IBE ratios than does FE capture after above-band-gap excitation. The smaller ratio for P_3^0 excitation indicates that excitons created in this excited state have sufficient excess energy that a sizeable fraction can overcome the barrier between A and P configurations before relaxing. This indicates that reconfiguration during FE capture may be a signifi-

TABLE I. Summary of the ratios of the luminescence decay prefactors I_{S0}/I_{L0} as a function of resonant excitation energy, luminescence monitoring line, and two different temperatures.

Excitation energy	Monitor P line 4.2 K	Monitor P line 1.4 K	Monitor R line 4.2 K	Monitor R line 1.4 K
$>FE_{TA}$	105	320	50	100
P_3^0	220	500		
P_2^0	1000	2300		
P_0^0			300	380

cant process. It is interesting to note that the very large ratios obtained by pumping P_2^0 are in fact consistent with a pure population of P-type IBE in the ground state just after the excitation pulse, followed by creation of a small population of A-type IBE by the reverse tunneling term τ_{PA}, with ΔE_2 taken to equal zero. On the other hand, the A component could also be generated by branching during relaxation, as occurs when pumping P_3^0. One would expect the largest I_{S0}/I_{L0} ratio when pumping directly into the P_0^0 ground state, but in this case the luminescence signal must be monitored using a replica of the P line such as R. It can be seen that pumping P_0^0 definitely increases I_{S0}/I_{L0} for the R line, but quantitative conclusions are difficult since I_{S0}/I_{L0} is different for the two lines under identical excitation conditions. Also, due to the weakness of the R line the spectrometer slits must be opened considerably, possibly admitting extraneous luminescence components.

In addition, several decay measurements were made while exciting the weaker features in the excitation spectrum. None of these resulted in I_{S0}/I_{L0} values smaller than those obtained for above-band-gap excitation, so we can conclude that none of the structure in the excitation spectrum is due to creation of A-type IBE. This indicates that either all transitions to A-type centers are very weak, or that ΔE_1 is large and only P-type bare binding centers exist at the temperatures in question.

VII. TIME-RESOLVED Si:In PHOTOLUMINESCENCE SPECTRA

The different I_{S0}/I_{L0} ratios obtained for the P and R lines in the preceding section suggest that the spectrum does not show a single decay behavior, as was at first thought to be the case.[19] In addition, strong variations in I_{S0}/I_{L0} were found in the region near the optical phonon replicas of the P line. To investigate this behavior, the computer-controlled multichannel scaling system was used to simultaneously collect a number of spectra at various delay times after above-band-gap excitation pulses. Some of the results are shown in Fig. 15.

The evolution of the spectrum after the excitation pulse is rather complicated. Figure 15(a) shows the short-time spectrum, collected between 0 and 0.25 ms after excitation, which is indistinguishable from a continuously excited spectrum. The principal features are the P line and its local mode replica R, along with the V and W lines and broad features related to the phonon density of states—* is associated with the TA branch, while ** is thought to be associated with the LA branch, and the structure labeled $O(\Gamma)$ and TO(W) is due to peaks in the optical phonon density of states.[16,29] Figure 15(b) shows an intermediate delay spectrum, taken between 0.25 and 1.25 ms after excitation. The broad phonon structure is seen to have increased in intensity relative to the P line, and two new lines labeled X and Y appear near the region of the optical phonon replicas of the P line. In addition, a new feature labeled Z appears as a small shoulder on the R line.

Figures 15(c) and 15(d) are spectra taken at 3.25—4.25 ms and at 6.25—9.25 ms after the excitation pulse, and are

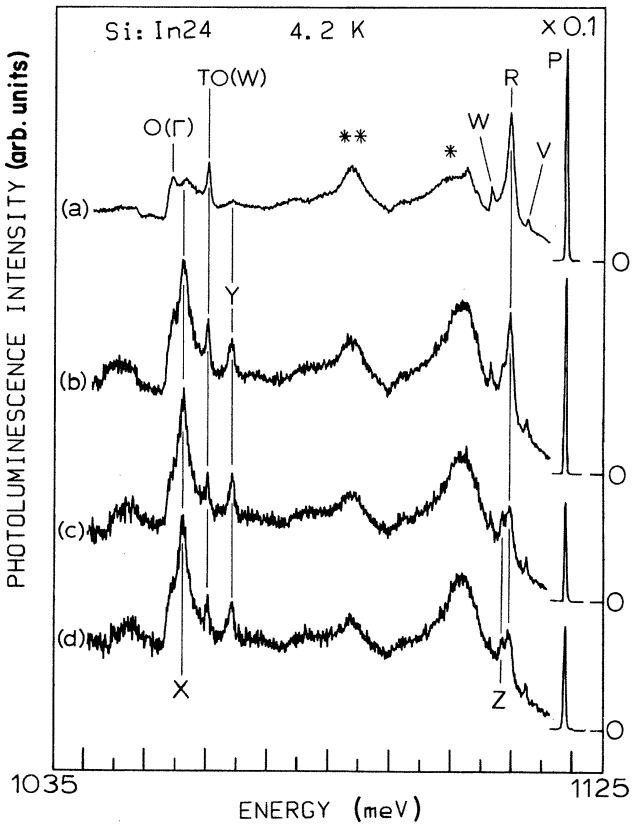

FIG. 15. Time-resolved Si:In spectra obtained with the photomultiplier detector, showing the change in the spectral features as a function of delay after the excitation pulse. The spectra correspond to windows of (a) 0.25—1.25 ms, (b) 1.25—2.25 ms, (c) 4.25—5.25 ms, and (d) 6.25—9.25 ms, relative to the excitation pulse. The data have been corrected for the detector response.

seen to be identical. At 4.2 K the spectrum ceases to change after about 1.5 ms and decays uniformly with the time constant τ_L. Similar time-resolved spectra were obtained at 1.4 K. Even at 7 K differences between the long and short delay spectra were discernible, while at 10 K and above, the spectra were identical at all delay times and decayed with a single 25-μs decay time.

It is tempting to propose that the change in the shape of the spectrum shown in Fig. 15 is due to the presence of a weak radiative decay channel for the A centers, which would become more apparent at long delay times, as the P-type spectrum decreases in intensity by a factor of 100 in the first millisecond. A problem with this interpretation arises from the fact that there are more than two types of transient behavior represented in the data of Fig. 15. A clearly visible example in Fig. 15 is given by the V to P intensity ratio, which changes by a small amount, while the X or Y to P ratio changes by a much larger amount. By subtracting a suitably scaled version of the $t=0$ spectrum shown in Fig. 15(a) from the long delay spectrum, with the scale factor chosen to null out the P line, one would expect to null out all $t=0$ features and be left only with the new long delay time features which could be ascribed solely to radiative A-center recombina-

tion. In fact, while this procedure effectively nulls out the dominant P and R lines, many $t=0$ features still remain (e.g., V, TO(W), $*$, $**$) due to the existence of more than two types of transient behavior as evidenced by Fig. 15. If the remaining features are ascribed to A-center luminescence, the fact that some of the $t=0$ features are not nulled would imply that the no-phonon line of the A centers exactly coincides with that of the P centers, and furthermore that the two systems couple to many of the same phonon modes (e.g., V, $*$, $**$). At present there is insufficient evidence to draw any firm conclusions regarding this rather complicated spectral behavior.

If the new lines X and Y are indeed related to radiative A-type IBE recombination, it is of interest to determine their origin. In the model used previously, both ΔE_1 and ΔE_2 were taken to be very small, which would locate the no-phonon A transition very near the P line. Another possibility could be that ΔE_1 was in fact very large and the Y line was the no-phonon A transition while X was a local mode replica of Y. To test this hypothesis, a delayed spectrum was taken using the Ge detector (which allows the observation of longer-wavelength photoluminescence) and a chopper wheel which only allowed the spectrometer to view the sample between 3 and 5 ms after the excitation pulse. The results are quite similar to the previous photomultiplier spectra above 1040 meV, and show none of the structure at lower energies which one would expect from a no-phonon transition located at X or Y. Thus we are left with the conclusion that although X and Y seem definitely related, and likely arise from radiative recombination of A-type IBE, their exact nature remains unknown.

VIII. CONCLUSIONS

In summary, we have demonstrated that the isoelectronic centers in Si:In and Si:Tl can be explained by a simple model in which the bound exciton can exist in one of two configurations, and that thermally activated rearrangement between these configurations accounts for the unusual transient and spectral behavior of these systems. Such behavior appears to be unique in the literature of bound-exciton defects. As yet we have no detailed explanation for the mechanism of this changeover, but it appears likely that the defect undergoes some kind of drastic structural rearrangement. Further elucidation of the changeover mechanism must await more detailed perturbative measurements.

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[1]See P. J. Dean and D. C. Herbert, in *Excitons,* edited by K. Cho (Springer, New York, 1979).

[2]J. Weber, W. Schmid, and R. Sauer, J. Lumin. 18/19, 93 (1979).

[3]J. Weber, W. Schmid, and R. Sauer, Phys. Rev. B 21, 2401 (1980).

[4]L. Canham, G. Davies, and E. C. Lightowlers, J. Phys. C 13, L757 (1980).

[5]M. O. Henry, E. C. Lightowlers, N. Killoran, D. J. Dunstan, and B. C. Cavenett, J. Phys. C 14, L255 (1981).

[6]N. Killoran, D. J. Dunstan, M. O. Henry, E. C. Lightowlers, and B. C. Cavenett, J. Phys. C 15, 6067 (1982).

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

[8]J. A. Rostworowski and R. R. Parsons, Can. J. Phys. 59, 496 (1981).

[9]G. S. Mitchard, S. A. Lyon, K. R. Elliot, and T. C. McGill, Solid State Commun. 29, 425 (1979).

[10]D. H. Brown and S. R. Smith, J. Lumin. 21, 329 (1980).

[11]M. L. W. Thewalt, U. O. Ziemelis, and R. R. Parsons, Solid State Commun. 39, 27 (1981).

[12]J. Weber, R. Sauer, and P. Wagner, J. Lumin. 24/25, 155 (1981).

[13]M. L. W. Thewalt, U. O. Ziemelis, S. P. Watkins, and R. R. Parsons, Can. J. Phys. 60, 1691 (1981).

[14]P. Wagner, J. Weber, and R. Sauer, Solid State Commun. 39, 1273 (1981).

[15]M. L. W. Thewalt, U. O. Ziemelis, and R. R. Parsons, Phys. Rev. B 24, 3655 (1981).

[16]R. E. Stahlbush and R. A. Forman, J. Lumin. 26, 227 (1982).

[17]J. Wagner, J. Weber, and R. Sauer, Solid State Commun. 39, 1273 (1981).

[18]J. Wagner and R. Sauer, Phys. Rev. B 27, 6568 (1983).

[19]S. P. Watkins, M. L. W. Thewalt, and T. Steiner, Solid State Commun. 46, 447 (1983).

[20]J. Weber, H. Buuch, and R. Sauer, Phys. Rev. B 25, 7688 (1982).

[21]S. P. Watkins, U. O. Ziemelis, M. L. W. Thewalt, and R. R. Parsons, Solid State Commun. 43, 687 (1982).

[22]T. N. Morgan, B. Welber, and R. N. Barghava, Phys. Rev. 166, 751 (1968).

[23]P. J. Dean, Phys. Rev. B 4, 2596 (1971).

[24]R. Sauer and J. Weber, *Proceedings of the 12th International Conference on Defects in Semiconductors, Amsterdam, 1982* (North-Holland, Amsterdam, 1983).

[25]U. O. Ziemelis and R. R. Parsons, Can. J. Phys. 59, 784 (1981).

[26]M. A. Vouk and E. C. Lightowlers, J. Lumin. 15, 357 (1977).

[27]R. Engleman and J. Jortner, Mol. Phys. 18, 145 (1970).

[28]D. V. Lang, Proceedings of the 15th International Conference on the Physics of Semiconductors, Kyoto, 1980 [J. Phys. Soc. Jpn. Suppl. A 49, 207 (1980).

[29]P. A. Temple and C. E. Hathaway, Phys. Rev. B 7, 3685 (1973).