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Lifetimes of Free and Bound Excitons in High-Purity GaAs

C. J. Hwang*

Bell Laboratories, Murray Hill, New Jersey 07974

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An analysis has been carried out for obtaining the free- and bound-exciton lifetimes from optical phase shifts measured on crystals with surface loss. It is found that the bound-exciton lifetime can be obtained directly from the measured phase shifts associated with the free- and bound-exciton lines, regardless of the surface condition. The optical phase shift of the free-exciton line from a "surface-free" crystal should be larger than that measured on the same crystal but with a lossy surface. Experiments to measure the phase shifts of free excitons and excitons bound to neutral and ionized donors (D^0 and D^+) and neutral acceptors (A^0) have been carried out and the various lifetimes have been determined from the above analysis. It was found that $\tau_{D0}=1.07\pm0.1$ nsec, $\tau_{D^+}=0.8\pm0.08$ nsec, and $\tau_{A0}=1.6\pm0.6$ nsec at 1.6 °K. The free-exciton lifetime decreases with increasing impurity concentration in the material (the longest lifetime obtained being 2.9 ± 1.3 nsec), indicating that the decay of free excitons is not governed by the direct annihilation of the electron-hole pairs.

I. INTRODUCTION

The edge emission around 1.5 eV in high-purity GaAs at low temperature (< 4.2 °K) consists of several sharp lines at 1.5157, 1.5141, 1.5133, and 1.5121 eV due to recombination of both free excitons and excitons bound to donors and neutral acceptors.[1-5] The stress dependence of the line position shows that the 1.5157-eV line is due to the decay of $n=1$ free excitons.[6,7] The line at 1.5141 eV has been identified as arising from the decay of excitons bound to neutral donors from the splitting behavior of the donor excited states in a magnetic field[4] and from the agreement[5] between the observed peak position and that expected from the electron-hole mass ratio recently calculated by Baldereschi and Lipari.[8] The decay of excitons bound to neutral acceptors has been shown from Zeeman experiments and from the temperature dependence of the line intensity[9] to be responsible for the emission at 1.5121 eV.[5] Although there has been no definite assignment of the origin of the 1.5133-eV line, it has been associated with the recombination of excitons bound to ionized donors simply because the line position is consistent with that expected from effective-mass considerations.[2,10] In this paper, measurements of lifetimes of these excitons are reported.

Information on the lifetimes is very useful in understanding the decay mechanism of the excitons. For example, dependence of free-exciton lifetime on impurity concentration indicates that free excitons decay through impurity trapping. Comparison of the measured lifetime with the theoretical lifetime will show the importance of nonradiative processes.[11] No measurements have been reported for the lifetimes of the above excitons in GaAs. This is perhaps not surprising, since these exciton lifetimes are extremely short (~ 1 nsec), which makes real-time decay experiments impractical (instrument limited). Furthermore, the requirement of high spectral resolution because of the location of several sharp lines in a small spectral region (~ 35 meV) means that one is working with a very weak detected signal in the usual optical-phase-shift techniques.[12,13] With an improved optical-phase-shift system reported earlier,[14] we are able to measure the phase shifts associated with the various exciton lines.

It has been demonstrated that the same crystal with and without surface recombination shows different measured phase shifts associated with the free-electron–hole recombination.[15,16] In the absence of any "surface-free"[17] crystals, it is necessary to carry out an analysis to show how the surface loss will affect the measured phase shifts and hence the lifetimes of the free and bound excitons. Such an analysis is shown in Sec. II. In Sec. III, the experiments are briefly described. Finally, in Sec. IV, the results are presented and discussed.

II. ANALYSIS OF OPTICAL-PHASE-SHIFT TECHNIQUE AS APPLIED TO MEASUREMENT OF FREE- AND BOUND-EXCITON LIFETIMES

In order to determine the lifetimes from the measured optical phase shifts (relative to the excitation light) associated with the free- and bound-exciton lines, we need to know the exciton-formation mechanism. We shall consider the case that the crystal is illuminated with a weak monochromatic light whose energy $\hbar\omega_0$ is greater than the energy gap E_g so that free electrons and holes are generated initially. In view of the observation of intrinsic oscillatory photoconductivity at 2 °K in similar crystals,[18] the excited electrons should lose energy rapidly through collision with longitudinal-optical phonons and then decay before losing additional energy by interaction with acoustic phonons. The energy to which the electrons relax before decay is $\mathcal{E} = (\hbar\omega_0 - E_g)/(1 + m_e^*/m_h^*) - q\hbar\omega_l$,[18] where $\hbar\omega_l$ is the optical-phonon energy and q is an integer such that $0 \leqslant \mathcal{E} \leqslant \hbar\omega_l$. Since the excited free holes do not contribute to the oscillatory photoconductivity, they should all be thermalized.[19]

The electrons must then decay from an energy $\mathcal{E}$ above the conduction-band edge and the holes from the valence-band edge either directly (free-electron–hole recombination; recombination at, or trapping by, impurities) or via the formation of free excitons which also decay subsequently by direct annihilation and impurity trapping. Experimentally, we have invariably observed the free-exciton line, but not the emission, due to free-electron–hole recombination in all high-purity crystals at 1.6 °K.[1–7,9,20] To infer the relative abundance of the free carriers and free excitons at the beginning of the excitation and the subsequent formation mechanism of the bound excitons from the above experimental observation, we need to know the radiative lifetimes of the free-carrier and free-exciton recombinations.

In the case of $\mathcal{E} = 0$, the radiative lifetime of the free carriers can be calculated from the method of van Roosbroeck and Shockley[21] using the experimentally measurable absorption spectrum. In the case of $\mathcal{E} \neq 0$ or lack of the absorption data for $\mathcal{E} = 0$, the radiative lifetime can still be calculated using the time-dependent perturbation analysis. Such an approach generally leads to a lifetime which is dependent on the concentration of the other type of carriers. Additional knowledge on the total lifetime of the carriers is required in order to obtain the radiative lifetime. The total lifetime can in principle be determined from the same phase-shift technique if the emission corresponding to the free-carrier recombination is observed. Unfortunately, no such emission has been seen in the luminescence measurements. Therefore, the radiative lifetime of the free-carrier recombination in the present case is calculated with a rather oversimplified model: the recombination of one electron at $\mathcal{E}$ above the conduction-band edge and one hole at the valence-band edge, an extreme case of weak excitation. The radiative lifetime τ_R for such a model has been derived previously and can be expressed (in the case of dipole approximation) as[22]

$$\tau_R = \frac{3m_0c^3}{2Ne^2\omega_{ul}f} \ , \tag{1}$$

where $f = 2(m_0\omega_{ul}/\hbar)\,|\vec{\gamma}|^2$ is the oscillator strength for the recombination, $|\vec{\gamma}|$ is the absolute value of the dipole matrix element, N is the refractive index, e is the electron charge, m_0 is the electron mass, c is the velocity of light, $\hbar\omega_{ul} = E_g + \mathcal{E}$ is the photon energy, and $\hbar$ is Planck's constant divided by 2π. It can be shown that Eq. (1) is also valid for such first-order processes as the decay of free and bound excitons. However, it may not be valid for the case of free-electron–hole recombination under conditions other than the above two-particle case. For the sole purpose of estimating the relative initial concentrations of free carriers and free excitons, the use of Eq. (1) is probably adequate.

Using $\omega_{ul} = 1.523$ eV, $N = 3.6$, and[23]

$$f = \tfrac{1}{12}[(m - m_e^*)/m_e^*][(E_g + \Delta E)/(E_g + \tfrac{2}{3}\Delta E)],$$

where m is the electron mass in vacuum, $m_e^* = 0.067m$[24] is the electron effective mass, $E_g = 1.521$ eV[25] is the energy gap, and $\Delta E = 0.33$ eV[26] is the spin-orbit splitting energy, we find that the radiative lifetime of the free-electron–hole recombination is ~ 3 nsec. The free-exciton-formation time and the trapping time of the free carriers must then be much less than 3 nsec.

Similarly, the radiative lifetime of the free-exciton recombination is found to be ~ 5×10^5 nsec by substituting in Eq. (1) the oscillator strength $f_{ex} = f\,|\phi_{ex}|^2\,\Omega = f(1/\pi a_{ex}{}^3)\Omega$,[27] where ϕ_{ex} is the wave function of the $n = 1$ exciton state, $\Omega = 45.18$ Å^3 is the volume of the unit cell in GaAs, and $a_{ex} = 139.5$ Å is the free-exciton radius. In order that the free-exciton emission can be observed, a very large portion of the generated free carriers (greater than $\frac{5}{3}\times10^5$:1) must form free excitons in a period of much less than 3 nsec. Since these free excitons must then decay either by direct annihilation or by impurity trapping, the major portion of the bound excitons is likely to come from trap-

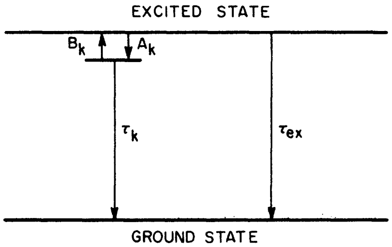

FIG. 1. Band diagram for the free- and bound-exciton states.

ping of free excitons instead of trapping of individual free electrons and holes at different stages of the excitation. In the following treatment, we shall therefore assume that the free-exciton formation time is infinitely short compared with the decay time, and that the bound excitons are formed entirely by trapping of free excitons.[11]

The exciton-band diagram consistent with the above picture is shown in Fig. 1. The ground state represents the state of the crystal when there is no optical excitation. States k denote various states associated with different impurity species (neutral donors, ionized donors, and neutral acceptors).

The one-dimensional continuity equations for the free and bound excitons can be written as

$$D\frac{\partial^2 n}{\partial x^2}+ge^{-\alpha x}-\frac{n}{\tau_{ex}}+\sum_k B_k n_k=\frac{\partial n}{\partial t}\ , \qquad (2)$$

$$A_k n-\frac{n_k}{\tau_k}=\frac{dn_k}{dt}\ , \qquad (3)$$

where D is the diffusion constant of the free excitons, g is equal to $\mathrm{Re}[g_0(1+me^{i\omega t})]$ in the optical-phase-shift technique[16] (m is the modulation index, g_0 is the generation rate when there is no modulation, and ω is the modulation angular frequency), α is the absorption constant of the excitation light, n is the free-exciton density, τ_{ex} is the free-exciton lifetime, B_k is the thermal ionization rate of the excitons from the bound state k to the free state, A_k is the capture rate of the free excitons by state k, τ_k and n_k are the lifetime and density of the bound excitons at state k, and x and t are the position and time variables. The free-exciton lifetime τ_{ex} as defined in Eq. (2), includes the trapping time by the various states k, and the radiative and nonradiative lifetimes associated with the free-exciton recombination. If $kT \ll E_k$(E_k is the binding energy of the bound exciton), as is the case in this experiment, then the term $\sum_k B_k n_k$ can be neglected in Eq. (2). The coupled differential equations (2) and (3) can then be solved analytically. Assuming a semi-infinite sample and that the surface loss can be described by a surface recombination velocity S through the boundary condition

$$D\frac{dn}{dx}\bigg|_{x=0}=Sn(0)\ , \qquad (4)$$

the solution for n_{ex} is

$$n_{ex}(x,t)=\mathrm{Re}\left(\frac{g_0\tau_{ex}}{1-\alpha^2L^2}f(L,\alpha,\tau_{ex},t)h(S/D,L,\tau_{ex},x)\right)\ , \qquad (5)$$

where $L=(D\tau_{ex})^{1/2}$ is the free-exciton diffusion length, and f and h are given by

$$f(L,\alpha,\tau_{ex},t)=1-\frac{me^{i\omega t}}{1+i[\omega\tau_{ex}/(1-\alpha^2L^2)]}\ , \qquad (6)$$

$$h(S/D,L,\tau_{ex},t)=e^{-\alpha x}-\frac{S+\alpha D}{(D/L)(i+i\omega\tau_{ex})^{1/2}+S}\times e^{-(x/L)(1+i\omega\tau_{ex})^{1/2}}\ . \qquad (7)$$

Since the absorption coefficient at the free-exciton wavelength is rather high (~ 10^4 cm^{-1}), the radiative recombination of the free exciton inside the crystal must suffer reabsorption before emerging out of the crystal. The detected free-exciton line intensity is then

$$I(\omega t)\propto\int_0^{\infty}\frac{n_{ex}(x,t)}{\tau_{exr}}e^{-\alpha' x}dx=\frac{1}{\tau_{exr}}\mathrm{Re}\left(\frac{g_0\tau_{ex}}{1-\alpha^2L^2}f(L,\alpha,\tau_{ex},t)H(S/D,L,\alpha,\tau_{ex})\right)\ , \qquad (8)$$

where α' is the absorption constant at the free-exciton wavelength and τ_{exr} is the radiative lifetime of the free excitons. The function $H(S/D, L, \alpha', \tau_{ex})$ is given by

$$H(S/D,L,\alpha',\tau_{ex})=\frac{1}{\alpha+\alpha'}-\frac{(SL/D+\alpha'L)L}{1+SL/D\,\alpha'L+(SL/D+\alpha'L)[\tfrac12(a+1)]^{1/2}+i\{\omega\tau_{ex}+[\tfrac12(a-1)]^{1/2}\}}\ , \qquad (9)$$

where $a=(1+\omega^2\tau_{ex}^2)^{1/2}$. The phase shift of the free-exciton luminescence relative to the excitation light is

$$\theta_{ex}=-\left(\tan^{-1}\frac{\omega\tau_{ex}}{1-\alpha^2L^2}+\tan^{-1}\frac{\omega\tau_{ex}+(SL/D+\alpha'L)[\tfrac12(\alpha-1)]^{1/2}}{(\alpha+\alpha')(SL/D+\alpha'L)\,L-\{1+(SL/D)\alpha'L+(SL/D+\alpha'L)[\tfrac12(\alpha+1)]^{1/2}\}}\right.$$
$$\left.+\tan^{-1}\frac{\omega\tau_{ex}+(SL/D+\alpha'L)[\tfrac12(\alpha+1)]^{1/2}}{1+(SL/D)\alpha'L+(SL/D+\alpha'L)[\tfrac12(\alpha+1)]^{1/2}}\right)\ . \qquad (10)$$

TABLE I. Lifetimes of free and bound excitons in high-purity GaAs. τ_{ex}, free-exciton lifetime; τ_{D^0}, lifetime of excitons bound to neutral donors; τ_{D^+}, lifetime of excitons bound to ionized donors; τ_{A^0}, lifetime of excitons bound to neutral acceptors.

Crystal	N_D[a](10^{14} cm^{-3})	N_A[a](10^{14} cm^{-3})	μ[b](10^5 cm^2/V sec)	τ_{ex}[c](nsec)	τ_{D^0}[c](nsec)	τ_{D^+}[c](nsec)	τ_{A^0}[c]
LD-043	5	3	1.28	2.9 ± 1.3	1.07 ± 0.1	0.8 ± 0.08	1.6 ± 0.6
LD-036	4.4	3.4	1.17	2.6 ± 0.4	0.78 ± 0.05	0.7 ± 0.05	1.35 ± 0.1
LD-031	7	4	1.13	1.7 ± 0.3	0.75 ± 0.05	0.7 ± 0.05	1.35 ± 0.1
LD-025	3.9	3.2	1.13	1.55 ± 0.3	0.75 ± 0.05	0.65 ± 0.05	1.2 ± 0.1
LD-023	7	5	1.04	1.13 ± 0.2	0.70 ± 0.05	0.6 ± 0.05	d

[a] Determined from 820-G Hall mobility: D. L. Rode (private communication).

[b] Measured at 77 °K.

[c] Measured at 1.6 °K.

[d] The line cannot be clearly resolved.

Thus, the experimentally measurable quantity θ_{ex} cannot give τ_{ex} unless the parameters D, S, L, and α' are known. The usual simplified relation $\theta_{ex} = -\tan^{-1}\omega\tau_{ex}$ holds only when $S \to 0$ (negligible surface loss) and $\alpha' \to 0$ (negligible reabsorption), or $L < 1/\alpha$ (very short diffusion length), regardless of the surface condition. In the latter case, the excitons generated within the absorption length decay in this region before they diffuse to the surface and are lost there. If $L \geqslant 1/\alpha$ and the surface loss cannot be ignored, τ_{ex} computed from the relation $\tau_{ex} = (1/\omega)\tan\theta_{ex}$ is shorter than that calculated from Eq. (10) for a given θ_{ex}. This has been observed experimentally using a "surface-free" sample to minimize the surface loss.[15]

It is easily seen that if there exists a finite free-exciton formation time, the measured phase shift θ_{ex} will be equal to the sum of the contributions from this formation time and the decay time. The free-exciton lifetime will be approximately equal to τ_{ex} determined from Eq. (10) minus the formation time. In other words, the free-exciton lifetime determined from the phase shift of the free-exciton line is an upper bound of the true free-exciton lifetime. As will be seen from Table I, if the formation time is less than 0.3 nsec, as is likely to be the case from the requirement that it has to be much less than 3 nsec, the error introduced in omitting it in the above treatment is within the experimental uncertainty of the present experiment.

The solution for the bound-exciton density can be obtained by substituting Eq. (4) in Eq. (2):

$$n_k(x,t) = \mathrm{Re}\left(\frac{A_i g_0 \tau_{ex}\tau_k}{(1+\omega\tau_k)(1-\alpha^2L^2)} \times f(L,\alpha,\tau_{ex},t)\,h(S/D,L,\tau_{ex},x)\right) . \quad (11)$$

Since the bound-exciton lines are below the free-exciton absorption line, the reabsorption of the bound-exciton recombination can be neglected. The bound-exciton-line intensity emerging from the crystal is then given by

$$I_k(\omega t) \propto \int_0^\infty \frac{n_k(x,t)}{\tau_{kr}}\,dx = \frac{1}{\tau_{kr}}\,\mathrm{Re}\left(\frac{A_i g_0 \tau_{ex}\tau_k}{(1+i\omega\tau_k)(1-\alpha^2L^2)} \times f(L,\alpha,\tau_{ex},t)\,H(S/D,L,\alpha'\tau_{ex})\right) , \quad (12)$$

where τ_{kr} is the radiative lifetime of the bound exciton at state k. The phase of the bound-exciton line is

$$\theta_k = -\tan^{-1}\omega\tau_k + \theta_{ex} , \quad (13)$$

and the bound-exciton lifetime is given by

$$\tau_k = (1/\omega)\tan(\theta_{ex} - \theta_k) . \quad (14)$$

Equation (14) is the same as that derived without consideration of surface recombination and photon reabsorption. A simultaneous measurement of the phase shifts of the free- and bound-exciton lines should then give the bound-exciton lifetime through the simple relation of Eq. (14), regardless of the surface condition and the effect of photon reabsorption of the free-exciton recombination. In other words, for a given crystal (or given τ_{ex} and τ_k), the effects of surface loss and photon reabsorption are to affect the measured θ_{ex} and hence θ_k, but not the difference of the two (the effects are substracted out). Furthermore, since both θ_{ex} and θ_k contain the same phase delay contributed by the free-exciton formation time, Eq. (14) also gives the true bound-exciton lifetime, regardless of whether the formation time can be neglected or not.

III. EXPERIMENTAL

The GaAs crystals were grown by liquid-phase epitaxy method described by Dawson.[28] They were grown on semi-insulating substrates from Ga solutions contained in quartz boats. Saturation of the melt with As was achieved by heating the Ga in contact with excess undoped GaAs source material at 700 °C for at least 1 h after thermal stabilization. The melt was then brought into contact with the substrate and cooled 20 °C at a rate of 10 °C/h. Following this cooling cycle, the substrate was separated from the melt and was then cooled to room temperature. All the crystals exhibit practically the same as-grown surface. They are *n*-type and all show mobility of greater than 10^5 cm^2/V sec at 77 °K.

Optical-phase-shift measurements were performed on the as-grown surface. The excitation is accomplished by the 4880-Å line of an Ar laser intensity modulated at a frequency of 104 MHz. The average laser power is about 7 mW. The spectral resolution is 0.4 meV for the free-exciton line and 0.1 meV for all the bound-exciton lines. The high resolution generally limits the rf signal strength available for photomultiplier detection. However, with an improved detection system described in Ref. 14, a good signal-to-noise ratio was obtained. The signal-to-noise ratio which determines the measurement accuracy was estimated from the swing amplitude of the phasemeter pointer.

IV. RESULTS AND DISCUSSION

A typical spectrum taken from our purest crystal (LD-043 in Table I) is shown in Fig. 2. The spectrum was obtained under constant photoexcitation, with the sample immersed in liquid He pumped to 1.6 °K. Due to the high purity of this crystal, the bound-exciton lines are reasonably well resolved. For slightly less pure crystals (LD-036, LD-031, LD-025, and LD-023 in Table I), the bound-exciton lines show considerable overlap. This is important since the measured bound-exciton lifetimes in these crystals will be affected by the contribution from the adjacent lines. Consequently, the bound-exciton lifetimes measured for the purest crystal should be regarded as the lifetimes closest to the true values. On the other hand, the free-exciton lifetime is resolved to a similar extent for all the crystals, resulting in a similar influence of the adjacent line on the free-exciton lifetime. It is therefore expected that the difference in the measured free-exciton lifetime is not due to the effect of a different degree of line overlap.

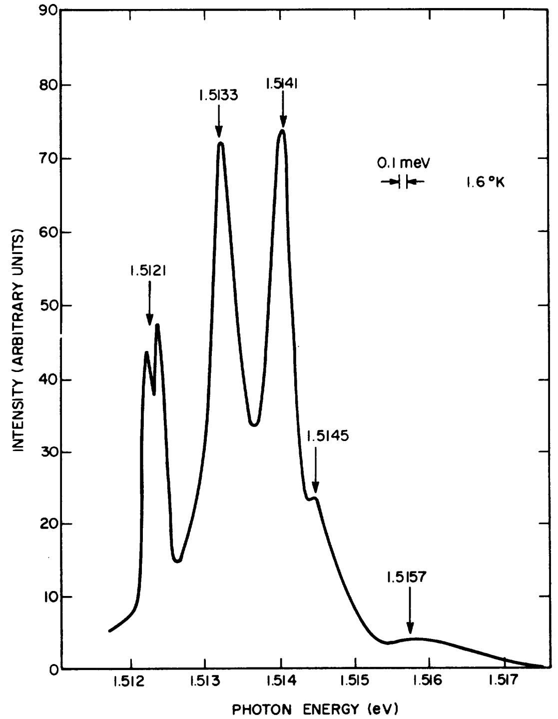

FIG. 2. Photoluminescence spectrum around 1.5 eV at 1.6 °K from a high-purity GaAs crystal grown from liquid-phase epitaxy technique.

In this phase-shift measurement, the 1.5145-eV line arising from the decay of excitons in the vicinity of neutral donors[4] from the background of the 1.5141-eV line could not be resolved nor could the doublet around 1.5121 eV be resolved, possibly because of the strong overlap or near-identical lifetimes. The lifetime of this doublet was measured with the spectrometer set at 1.5121 eV.

In order to determine the free-exciton lifetime τ_{ex} from the measured θ_{ex}, knowledge of the values of S/D, α, α', and L are required. Although these parameters were not measured, their values are available in the literature. The values of $\alpha = 1.1 \times 10^5$ cm^{-1} and $\alpha' = 1.1 \times 10^4$ cm^{-1} are obtained from Sturge's absorption data.[25] The value of $L = 0.3 \pm 0.05$ μ has been deduced by Leite and Shah[29] from analysis of photoluminescence spectra taken on similar epitaxial layers having different thicknesses on an identical substrate. A value of $SL/D \simeq 5$ (or $S/D \simeq 1.7 \times 10^5$ cm^{-1}) may be inferred from the analytical method of Laff[30] and the photoconductivity data of Nahory.[31] The free-exciton line shape obtained from correction of the theoretical line shape using these values for L and S/D has been shown to agree quite well with the observed one.[32]

The width of the surface depletion layer as calculated from the above L and S/D is about 0.15 μ.[32] Since this is smaller than the exciton diffusion length L, it is expected that any effect caused by the depletion layer on θ_{ex} will be small. Furthermore, it has been demonstrated that the major effect of the depletion layer is to distort the observed free-exciton spectrum because of reabsorption by a medium with a different absorption constant.[32] The absorption constant in this region was found to be about 2×10^4 cm^{-1} at the free-exciton wavelength,[32] a value slightly different from 1.1×10^4 cm^{-1} used for the whole crystal in our calculation. Actual calculation using Eq. (9) shows that the deviation of τ_{ex} resulting from this difference is small compared with the uncertainty caused by the signal-to-noise consideration. Hence, the effect of surface depletion region on the measured free-exciton lifetime will be neglected.

Figure 3 is a plot of θ_{ex} as a function of τ_{ex} as given by Eq. (9), using the above values for α, α', L, and S/D. The function $\tau_{ex} = (1/\omega) \times \tan\theta_{ex}$ is also plotted for comparison. In order to see how sensitive τ_{ex} is to the variation of S/D, two curves are shown which correspond to deviations of S/D of one order of magnitude larger and smaller than the estimated value of 1.7×10^5 cm^{-1}. Even for this rather high uncertainty in S/D, the uncertainty in τ_{ex} is less than 40% (the measured θ_{ex} for all the crystals are less than 40°), which is comparable to the uncertainty caused by the signal-to-noise consideration. Since it is unlikely that error in S/D will be as high as one order of magnitude, as a rule the effect of uncertainty in S/D on τ_{ex} is neglected. The errors shown in Table I are, therefore, all due to signal-to-noise consideration. The value of τ_{ex}, when taking into account the surface loss and photon reabsorption, is always longer than would be predicted from the relation $\tau_{ex} = (1/\omega)\tan\theta_{ex}$, in agreement with the experimental observation of Keune *et al.*[15]

The various lifetimes determined from Eqs. (1) and (2) are shown in Table I for several crystals. It is seen that τ_{ex} decreases with decreasing purity of the crystals, indicating that the radiative free-exciton recombination is not the dominant mechanism. This is consistent with the calculation that the free exciton has a very long radiative lifetime and with the observation that the free-exciton-line intensity is much weaker than any of the bound-exciton lines. As expected, the bound-exciton lifetime for each crystal is somewhat different because of differences in the degree of the adjacent line overlap. For the purest crystal, the shortest lifetime of 0.8 ± 0.08 nsec is associated with the decay of excitons bound to ionized donors, and the longest lifetime of 1.6 ± 0.6 nsec is associated with excitons bound to neutral acceptors. No modulated photoluminescence signals were detected for the four lines in the neighborhood of 1.49 eV, where Rossi *et al.*[33] and Brantley *et al.*[34] have associated four lines with ionized acceptors. This means that the sum of the exciton trapping and decay times is greater than 9.6 nsec, which is the repetition period of the modulated excitation light.

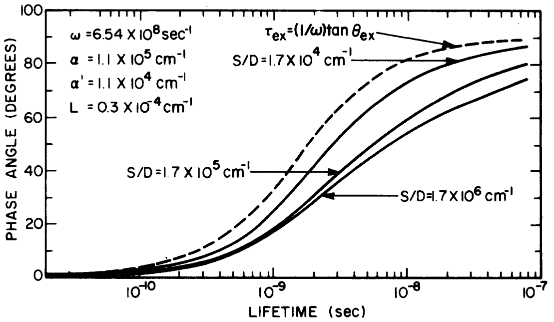

FIG. 3. Effect of surface recombination on the variation of phase shift with respect to the free-exciton lifetime. The effects of carrier diffusion and photon reabsorption are included.

Further insight into the free- and bound-exciton decay processes can be obtained from Table I. First, we note that all the bound excitons decay at a faster rate than the free excitons. Second, since the trapping time of the excitons by each impurity species (neutral and ionized donors, and neutral acceptors) is longer than the free-exciton decay time, the formation rate is smaller than the annihilation rate for any kind of the above bound excitons.

It has been suggested from the temperature dependence of the line intensity that Auger recombination is important in the decay of excitons bound to neutral donors.[2] Our data and a calculation using the theory of Rashba and Gurgenishvili[35] for the radiative lifetime show that this is not the case.[11] This result has also been found in CdS for an exciton bound to a shallow neutral donor.[11] It indicates that for a shallower donor, since both the electron and the bound-exciton radii are larger, the probability for collision between the exciton and the electron is smaller, resulting in a less efficient Auger process.

V. CONCLUSION

We have shown that the optical-phase-shift technique can yield directly the true bound-exciton lifetime regardless of the sample surface condition if the phase shifts associated with the free- and bound-exciton lines can be measured simultaneously. It is also shown that the true exciton lifetime is longer than would be predicted from the relation $\tau_{ex} = (1/\omega)\tan\theta_{ex}$ for lossy surface. Direct free-exciton annihilation is seen not to be the dominant mechanism in the free-exciton decay process. The bound excitons decay faster than the free excitons, and the trapping rates of free excitons by various impurity states are slower than the corresponding decay rates.

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[*] Present address: Hewlett Packard Laboratories, Palo Alto, Calif. 94304.

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Pseudopotential Theory of Shallow-Donor Ground States

Daniel Schechter

Department of Physics-Astronomy, California State University at Long Beach, Long Beach, California 90840

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The effective-mass theory of shallow impurity states is given a pseudopotential formulation. A first-principles pseudopotential is constructed accounting for orthogonalization to the impurity core states, spatial dependence of the dielectric constant, and the spatial dependence of the core shielding. Valley-orbit coupling is included, and a correction is made for the energy shift due to the deformation produced by the size difference of the host and impurity atoms. A variational calculation is done for the ground states of P, As, and Sb in Si, and good results are obtained for the lowest ground states (A_1) of P and Sb, poor results for As.

I. INTRODUCTION

The effective-mass theory of shallow impurities given by Kohn and Luttinger[1] agrees well with experiment in the case of the impurity excited states.[2-6] However, there is serious disagreement between theory and experiment in the case of the impurity ground states. The energy levels as determined by far-ir spectroscopy,[7] $|\psi(0)|^2$ as measured by EPR,[8] and also $|\psi(\vec{r}_l)|^2$ as found by electron-nuclear-double-resonance experiments,[8,9] are all poorly predicted by effective-mass theory.

One of the difficulties with the effective-mass theory is that it breaks down if the potential varies rapidly. This is precisely what happens when one tries to account for various central-cell effects,[10] as must be done for the ground state. Morita and Nara[11] have circumvented this difficulty in the case of donors in Si by dividing space about the impurity into two regions. In the outer region, effective-mass theory is valid and in the inner region the complete Schrödinger equation is used, rather than effective-mass theory. They take account of the spatial variation of the dielectric constant, the differing spatial dependence of the core shielding of the host atom and the various impurity atoms, the local distortion of the lattice due to the different size of the host and impurity atoms, of orthogonalization of the impurity wave function to