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Reaction kinetics in GaP:(Zn,O)

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Photoinduced reactions in which pairs of $\mathrm{Zn_{Ga}}$ and $\mathrm{O_P}$ ions in GaP dissociate and subsequently re-form are studied. The decay of nearest-neighbor (Zn,O) pair luminescence is measured versus laser power and temperature. The dissociation rate of the pairs is deduced with the use of a model for the electron-hole recombination kinetics which includes the effects of saturation and spatially dependent carrier generation. The activation energy for the photoinduced dissociation is found to be 0.60 ± 0.07 eV. Dissociation of the nearest-neighbor pairs by purely thermal mechanisms is also observed, with an activation energy of 2.6 ± 0.6 eV. From these activation energies and the observed pre-exponential factors, the photoinduced dissociation is determined to be a recombination-enhanced defect reaction. The dissociated nearest-neighbor pairs tend to re-form as pairs with small inter-ion separation.

I. INTRODUCTION

The properties of gallium phosphide doped with zinc and oxygen have been extensively studied, primarily because of the use of this material in light-emitting diodes. These diodes are observed to degrade under forward-bias operation.[1-3] In a previous paper,[4] we have shown that this degradation is due to the dissociation of nearest-neighbor $(\mathrm{Zn,O})_{m=1}$ pairs. When the GaP is subjected to laser excitation, we observe luminescence from radiative electron-hole recombination at the $(\mathrm{Zn,O})_m$ pairs, where m refers to an mth-nearest-neighbor pair. At elevated temperatures, the nearest-neighbor pair luminescence intensity decreases with time due to the dissociation of the pairs. After the nearest-neighbor pair dissociates, it re-forms as a further separated pair. In this paper, we will examine the kinetics of this reaction. The word "kinetics" here has a twofold meaning: First, we will discuss the electron-hole recombination kinetics in order to relate the observed photoluminescence intensities with the impurity concentrations. Second, we will study some aspects of the kinetics of the atomic diffusion process in which the $(\mathrm{Zn,O})_{m=1}$ pair dissociates and later re-forms as a further separated pair $(\mathrm{Zn,O})_{m>1}$.

The major result of this work is that the $(\mathrm{Zn,O})_{m=1}$ dissociation is a "recombination-enhanced" reaction in which energy available from electron-hole recombination is transferred to localized vibrational modes which leads to the dissociation. This type of reaction has not previously been observed in a system which is as well characterized as GaP:(Zn,O). Thus, this system provides a good opportunity for studying the strong electron-phonon interaction which is often present at "deep-level" defects in semiconductors. The understanding of this interaction is important since it significantly affects the performance of semiconductor devices.[5,6]

Photoluminescence (optical emission) data will be presented throughout this paper, and some experimental details are summarized in Sec. II. In Sec. III, equations are written describing the electron-hole recombination kinetics. We explicitly include the effects of saturation of the $(\mathrm{Zn,O})_m$ electron occupation, and of spatially varying electron-hole generation. Several limits of these equations that are applicable to the experiments described here will be discussed. Simple relations between the observed photoluminescence intensities and the defect concentrations are derived. Using these relations, we present in Sec. IV of this work an analysis of the decay rates of the $(\mathrm{Zn,O})_{m=1}$ luminescence intensities. The observed decay rates are shown to be proportional to the electron occupation of the pairs. At high laser powers the decay rates saturate and equal the dissociation rate of the pairs. From the temperature dependence of the dissociation rates, activation energies for the reactions are deduced. We show that the $(\mathrm{Zn,O})_{m=1}$ pairs can dissociate by a recombination-enhanced process, or by purely thermal mechanisms.[7] In Sec. V, data are presented on the distribution of $m>1$ pairs that are formed by the dissociation of the $m=1$ pairs. A brief discussion is given of the process by which the Zn and O impurities diffuse through the lattice to form the $(\mathrm{Zn,O})_{m>1}$ pairs. The observed degradation rates are shown to be dependent on the details of this diffusion process. The conclusions which can be drawn from this work are presented in Sec. VI.

II. EXPERIMENTAL

The samples used in this work were liquid-phase-epitaxially grown *p-n* junctions on *n*-type GaP (single crystal). The growth technique is described by Saul, Armstrong, and Hackett.[8] The exposed 50-μm thick layer of the junction is *p* type, doped with Zn and O. The (substitutional) O concentration is about 10^{16} cm^{-3} and the Zn concentration is about 3×10^{17} cm^{-3} (based on crystal-growth conditions). Other impurities include N and S. The photoluminescence spectra were obtained using a liquid-N_2-cooled *S*-1-type photomultiplier and a SPEX 1269 spectrometer with a 1200 lines/mm grating blazed at 1 μm. For the low-temperature work ($T<100$ K) reported here the sample was mounted in a variable-temperature cryostat and illuminated with the 4545-Å line of an Ar^+ laser. The sample was moved vertically to permit observation of different regions of the crystal and the change in photon collection efficiency between these runs was very small. For the high-temperature work (300 K $<T<$ 700 K) the sample was mounted on a heating block and illuminated with the 4880-Å line of an Ar^+ laser, focused to a beam diameter of 55 μm full width at half maximum (FWHM). The maximum sample heating ΔT can be estimated from

$$\Delta T=\frac{P}{2\pi k\sigma} \tag{1}$$

where P is the absorbed laser power, k is the thermal conductivity [$k=0.4$ W/cm K at 473 K for GaP (Ref. 9)], and σ is the beam width [FWHM equal to $2\sigma\sqrt{(2\ln 2)}$]. This formula is derived by solving the heat-diffusion equation in an infinite slab of thickness l with one side at a constant temperature and the other side exposed to a surface heat source with a Gaussian profile in the limit $\sigma<<l$. For a typical power level of $P=200$ mW we find $\Delta T=35$ K. For the results reported here the sample was in air, although similar results were obtained when the sample was in a He environment. Annealing studies ($T>1000$ K) were performed in a furnace purged with He. Following each anneal the sample was quenched in water and etched for 3 min in 3:1:1 H_2SO_4:H_2O_2:H_2O at 60 °C.

III. ELECTRON-HOLE RECOMBINATION KINETICS

The kinetics of electron-hole recombination in GaP:(Zn,O) have been extensively studied.[10–16] It is not the purpose of this work to obtain a detailed understanding of the recombination kinetics. Rather, we wish to arrive at approximate values for some of the kinetic parameters. From these values we will determine the regime of carrier concentrations in which our experiments lie, and this will enable us to make a reasonable interpretation of the data to be presented in Secs. IV and V.

We use a simple but accurate model which is similar to that used for nearest-neighbor pairs by Henry, Bachrach, and Schumaker.[16] Each $(\mathrm{Zn,O})_m$ center is considered to be a single-electron trap, with an associated electron release rate R_m, capture rate C_m, and a total recombination rate $1/\tau_m$. For $m\rightarrow\infty$, i.e., isolated oxygen, a second electron level has been observed.[5] Here we will be considering centers with $m<50$ for which this level has not been observed and so we will ignore it. For the present discussion, the hole occupation of the $(\mathrm{Zn,O})_m$ centers will be implicitly included in the electron recombination rate $1/\tau_m$. Later, we will consider the dependence of $1/\tau_m$ on the various hole concentrations. The concentration n_m of $(\mathrm{Zn,O})_m$ centers which are occupied by electrons is given by

$$\frac{dn_m}{dt}=-\frac{n_m}{\tau_m}-R_m n_m+C_m(N_m-n_m)n_0\,,\qquad m=1,2,3,\ldots\,, \tag{2}$$

where N_m is the total concentration of $(\mathrm{Zn,O})_m$ centers and n_0 is the free-electron concentration. In steady state, the concentration of occupied $(\mathrm{Zn,O})_m$ centers is found by equating Eq. (2) to zero to yield

$$f_m\equiv\frac{n_m}{N_m}=\frac{n_0/n_{tm}}{1+n_0/n_{tm}}\,, \tag{3a}$$

where

$$n_{tm}\equiv\frac{1/\tau_m+R_m}{C_m}\,. \tag{3b}$$

Here, f_m represents the fractional electron occupation of the centers. The intensity of luminescence emitted from an mth-nearest-neighbor pair is given by

$$I_m = \frac{1}{\tau_m^{\text{rad}}} n_m = \frac{1}{\tau_m^{rad}} N_m f_m \;, \tag{4}$$

where $1/\tau_m^{\text{rad}}$ is the radiative decay rate. Later in this work we will discuss processes in which the impurity concentrations N_m vary with time. However, these time variations are very slow compared with those expressed in Eq. (2); therefore Eq. (3) is still valid at each point in time.

Let us consider the minority-carrier (electron) concentration n_0. The variables of interest in these experiments are the laser power P, the temperature T, and the impurity concentrations N_i. The impurities labeled N_i include the $(\text{Zn,O})_m$ centers as well as various intrinsic impurities that could be undergoing photoinduced reactions.[3,17] In steady state n_0 is in general a function of T, P, and N_i. Neglecting spatial diffusion of the carriers we write

$$n_0 = G\tau_0 \;, \tag{5}$$

where G is the electron-hole generation rate and τ_0 is defined by this equation to be the steady-state minority-carrier lifetime. We will assume that τ_0 has no spatial dependence. This neglects effects such as surface recombination. The spatial dependence of G is derived by considering the incident laser beam that is perpendicular to the surface (x,y plane) of the crystal. The photon density has a Gaussian dependence on $\rho = [(x^2+y^2)]^{1/2}$ and varies exponentially with z (the direction into the crystal). Thus, the generation rate can be expressed

$$G = \frac{\alpha P}{h\nu_i 2\pi\sigma^2} \exp\left[\frac{-\rho^2}{2\sigma^2} - \alpha z\right] , \tag{6}$$

where P is the absorbed laser power, $1/\alpha$ is the absorption depth, σ is the beam radius, and $h\nu_i$ is the incident photon energy. The minority-carrier lifetime τ_0 is determined by all of the various recombination channels in the material. In our experiments we observe quantities which are independent of τ_0, and so we do not need to know its precise value. The minority-carrier concentration can be estimated by observing the luminescence intensity as a function of laser power.[11] For the nearest-neighbor pairs at $T = 500$ K we observe a significant saturation effects ($f_1 \approx 0.5$) to begin at $P = 100$ mW (FWHM $= 55\ \mu$m). At this temperature $1/\tau_1 \approx 10^6\ \text{s}^{-1}$ (Ref. 16) $< < R_1 \approx 10^8\ \text{s}^{-1}$ (Ref. 14). The maximum minority-carrier concentration is then given by $n_0 \approx n_{t1} \approx R_1/C_1 \approx 5\times10^{15}\ \text{cm}^{-3}$. This also equals the concentration of majority carriers (holes) introduced by the laser. From Eqs. (5) and (6) this value of n_0 corresponds to a lifetime of $\tau_0 \approx 1$ ns, which seems quite reasonable.

Much of the complicated electron-hole recombination kinetics has been hidden in the rates $1/\tau_0$, $1/\tau_m$, and $1/\tau_m^{\text{rad}}$. The rate of $1/\tau_m$ is the sum of nonradiative and radiative rates. There are two nonradiative decay channels: Auger decay[14] and multiphonon-emission (MPE) recombination.[5] There are also two radiative decay channels: The bound electron can recombine with a hole bound onto the same $(\text{Zn,O})_m$ center, or with a hole bound onto a distant impurity, namely, a Zn acceptor.[10,18] The rates $1/\tau_m$ and $1/\tau_m^{\text{rad}}$ are therefore functions of the temperature and various hole concentrations. The concentration of holes introduced by the laser is small compared with the free-hole concentration of $p \approx 10^{17}\ \text{cm}^{-3}$ for $T \gtrsim 300$ K. Furthermore, at these temperatures the shallowly bound holes are in equilibrium with the free holes.[15,16] Thus, $1/\tau_m$ and $1/\tau_m^{\text{rad}}$ will be functions only of temperature and will have very little spatial or time dependence.

Now let us specialize to the experiments described here. For ease of discussion we separate these into two cases. First we consider the high-temperature results which will be presented in Sec. IV. In these experiments the sample is exposed to the laser at some temperature $300\ \text{K} < T < 700$ K and some laser power P. The intensity of $(\text{Zn,O})_{m=1}$ luminescence is observed to decrease with time, presumably due to some changing impurity concentration N_i. The luminescence intensity is given by

$$I_1(t) = \frac{1}{\tau_1^{\text{rad}}} \int dV\, N_1(\rho,z,t) f_1(\rho,z,t) \;, \tag{7}$$

where the spatial dependence of f_1 is given by Eqs. (3a), (5) and (6). At low power levels the electron occupation f_1 is proportional to the minority-carrier concentration n_0. In general, n_0 changes with N_i and results in changes in the $(\text{Zn,O})_{m=1}$ luminescence intensity. We have observed these effects. At low powers a change in n_0 will cause the entire luminescence spectrum to change uniformly. However, at high powers the luminescence band saturates; $f_1 \rightarrow 1$ for most of the centers contributing to the band. In that case the luminescence intensity is independent of n_0. The observed decreasing intensity is due to a decreasing concentration of $(Zn,O)_1$ pairs, and the intensity is directly proportional to the pair concentration. The data presented in Sec. IV is in this high-power regime.

The second case to discuss are the low-temperature results presented in Sec. V. Here we observe luminescence from different regions of a sample which have different pair concentrations N_m. Care was taken to keep the temperature, laser power, and photon collection efficiency constant between the different regions. The luminescence intensity from various shallow impurities is observed to be identical in the regions, so that the electron and hole concentrations are probably constant. This implies that f_m and $1/\tau_m^{\text{rad}}$ are constant. Therefore, from Eq. (4), the ratio of luminescence intensities equals the ratio of pair concentrations in the different regions.

IV. REACTION RATES

In Fig. 1 we show several high-temperature photoluminescence spectra. As discussed in our previous publication[4] these spectra consist of a band centered at 1.7 eV due to nearest-neighbor $(Zn,O)_{m=1}$ pairs, and a band centered at 1.5 eV due to further separated pairs $(Zn,O)_{m>1}$. There is also luminescence at 2.1 eV due to various shallow impurities and possibly free-exciton or band-to-band recombination. In Fig. 1 the time between successive scans is about 30 min. We see that the intensity of the $(Zn,O)_{m=1}$ luminescence is decreasing and the intensity of the $(Zn,O)_{m>1}$ luminescence is increasing. For the high laser power used in Fig. 1 the $m=1$ and $m>1$ bands are saturated (at least initially, see below), and so their changing intensities are due to changing pair concentrations. Clearly the nearest-neighbor pairs are dissociating at some rate, and further-separated pairs are forming at the same rate. We refer to this reaction as an "aging" process. This reaction was first studied in luminescence by Dapkus and Henry[2] and was identified in our previous paper.[4]

The $(Zn,O)_{m=1}$ dissociation reaction is not a thermal one, since the temperature in Fig. 1 is only 470 K (sample heating due to the laser is about 20 K), and the $(Zn,O)_{m=1}$ pairs are thermally stable up to 800 K. Rather, the reaction is photoinduced.[2] The incident light creates electron-hole pairs in the material, and the electrons and holes may be captured and may recombine at the (Zn,O) centers. The energy to dissociate the $(Zn,O)_{m=1}$ pairs comes from some electron (or hole) capture or recombination event at the defect. In our previous work[4] we identified this event to be electron-hole recombination. Here, we will give a detailed

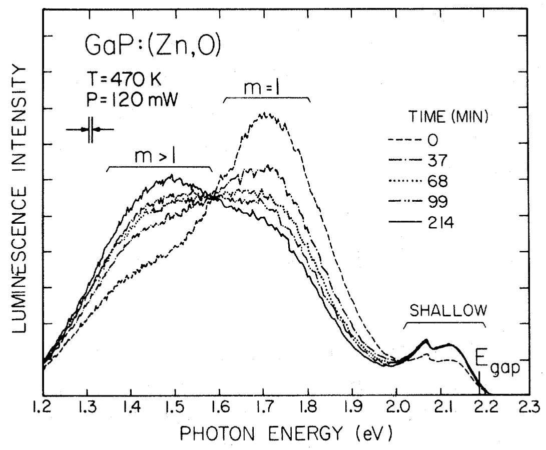

FIG. 1. High-temperature photoluminescence spectra from (Zn,O) donor-acceptor pairs. The labels m denote luminescence from an mth-nearest-neighbor pair. Several successive scans are shown. The luminescence intensities are changing with time, indicating defect reactions in progress.

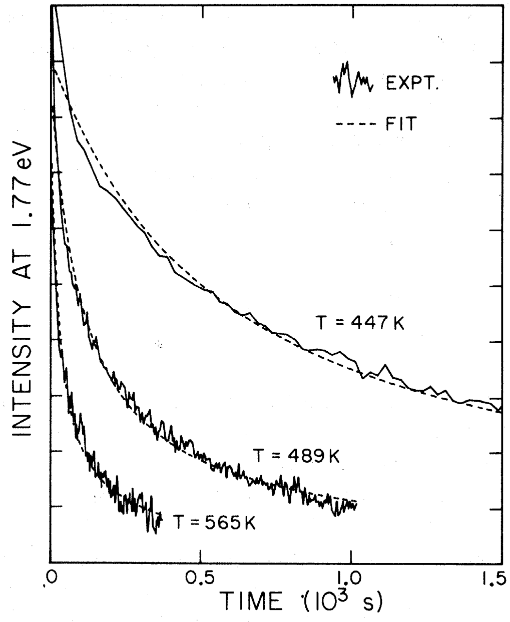

FIG. 2. Decay of the nearest-neighbor $(Zn,O)_{m=1}$ luminescence at various temperatures T. The data were fitted to a theoretical form corresponding to the $f(0,0)\rightarrow 0$ curve shown in Fig. 3.

account of how we arrived at this identification.

The decay (intensity versus time) of the $(\mathrm{Zn,O})_{m=1}$ luminescence is nonexponential. Figure 2 shows several decay curves. Typically, the luminescence intensity initially changes relatively fast, then it slows down to a long-lived tail. We attribute this nonexponential behavior to a nonuniform minority-carrier (electron) density in the material. This nonuniformity is due to the Gaussian profile of the incident laser beam and the exponential dropoff of its intensity into the sample. A nonuniform electron density results in a nonuniform electron occupation of the $(\mathrm{Zn,O})_1$ centers. Those centers with high occupation ($f_1 \rightarrow 1$) dissociate at some rate, and those centers with low occupation ($f_1 \rightarrow 0$) dissociate at a much slower rate. The observed decay curves are integrals over the sample of all the individual exponential decays. The result is a nonexponential decay. For high laser powers the observed luminescence is initially due almost entirely to the saturated centers. In that case the luminescence intensity is proportional to the pair concentration and independent of n_0, as discussed in Sec. III. At later times we observe those centers whose occupation is lower. Then, the luminescence intensity may depend on n_0. We can monitor n_0 by observing the intensity of luminescence from the shallow impurity levels. As shown in Fig. 1, the variation in n_0 occurs over a much shorter time period than the $(\mathrm{Zn,O})_{m=1}$ decay time. We observe that this is true for $P \gtrsim 100$ mW at all of the temperatures discussed here. Thus, the final part of the decay curves are not affected by n_0 because it is a constant. Therefore, we need not further concern ourselves with the time dependence of n_0 or f_1.

The degradation observed by Henry and Dapkus[3] is also reported to be nonexponential. In their case the degradation was accomplished using forward biased *p-n* junctions in which the minority-carrier concentration varies exponentially with distance from the junction. This produces nonexponential degradation characteristics similar to those reported here. Another example of nonexponential behavior is seen in carrier capture or emission rates as observed in deep-level transient spectroscopy (DLTS).[19,20] The carrier capture rate is proportional to the free-carrier density. This density is spatially varying at the edge of the depletion region. The resulting capture curves are nonexponential with a long-lived tail on them.[21] However, with a large enough reverse bias, the size of the depletion region is large compared with the edge region, and these effects can be minimized. In our experiments the laser power is never large enough to produce an essentially uniform excitation region, and so the nonexponential effects are always significant.

Let us now derive a functional form for the observed decay curves. From Eqs. (2)–(6) we find that the electron occupation of the $(\mathrm{Zn,O})_1$ centers is given by

$$f(\rho,z)=\frac{f(0,0)\exp\left[\dfrac{-\rho^2}{2\sigma^2}-\alpha z\right]}{1+f(0,0)\left[\exp\left[\dfrac{-\rho^2}{2\sigma^2}-\alpha z\right]-1\right]}\ , \tag{8}$$

where we have dropped the subscript 1. We assume that the dissociation rate of a given center is proportional to its occupation. This assumption is justified below. Thus, the concentration of $(\mathrm{Zn,O})_1$ centers at (ρ,z) varies with time according to

$$N(\rho,z,t)=N(0)\exp[-f(\rho,z)rt]\ , \tag{9}$$

where r is the reaction rate and $N(0)$ is the spatially uniform impurity concentration at $t=0$. We are now ready to derive the main theoretical result of this paper: the time dependence of the $(\mathrm{Zn,O})_1$ luminescence intensity in a model where the pairs are dissociating at a rate proportional to their spatially dependent electron occupation. From Eqs. (7)–(9) the total intensity of $(\mathrm{Zn,O})_1$ luminescence is evaluated to be

$$I(t)=\frac{N(0)f(0,0)\sigma^2}{\tau_1^{\mathrm{rad}}\alpha}\int_0^1 du\,\ln\left[\frac{1}{u}\right]\frac{\exp\left[\dfrac{-f(0,0)urt}{1+f(0,0)(u-1)}\right]}{1+f(0,0)(u-1)}\ . \tag{10}$$

Figure 3 shows several examples of Eq. (10) for various values of $f(0,0)$. For $f(0,0)\rightarrow 1$ the decay is purely exponential. This corresponds to an infinitely large excitation region with uniform occupation of all the centers. For $f(0,0)\rightarrow 0$ the decay follows an exponential integral form. In our experiments $f(0,0)<0.9$. From Fig. 3 we see that Eq. (10) is quite well approximated by its $f(0,0)\rightarrow 0$

limit,

$$I(t)\approx\frac{a}{r_0t}[\gamma+\ln(r_0t)+E_1(r_0t)]+b\ ,\qquad(11)$$

where a is a constant, γ is Euler's constant, $r_0=f(0,0)r$ is the observed decay rate, and E_1 is an exponential integral of the first kind. To this form we have added another constant b to account for the background intensity due to $(\mathrm{Zn,O})_{m>1}$. Equation (11) provides a good fit to all of the observed decay curves. This is the real justification for using it.

The data shown in Fig. 2 were fitted to the functional form Eq. (11). The decay curves shown in the figure have had a background intensity b (determined from the fit) subtracted from them. The decay rates determined from the fits are plotted in Fig. 4 versus the incident laser power. At low powers the rates increase linearly with power; at high powers the rates approach some limit: the saturated decay rate. The decay rates saturate when the electron occupation saturates. This justifies the above assumption that the dissociation rate is proportional to the electron occupation. The saturation power level increases with temperature as expected from Eq. (3b). The fact that the decay rates do indeed saturate provides evidence that sample heating and large hole concentrations due to the laser excitation are not significantly affecting our results.

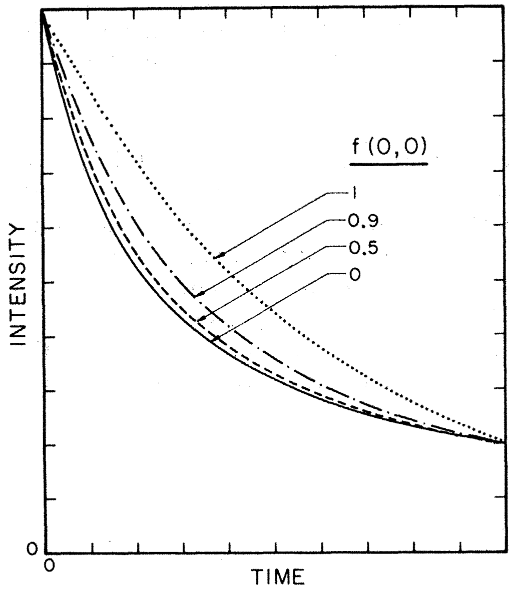

FIG. 3. Theoretical curves for the decay of the $(\mathrm{Zn,O})_{m=1}$ luminescence. $f(0,0)$ is the maximum electron occupation of the centers. $f(0,0)\rightarrow 1$ for very large laser powers and $f(0,0)\rightarrow 0$ for small laser powers. For the experiments described here, $f(0,0)<0.9$.

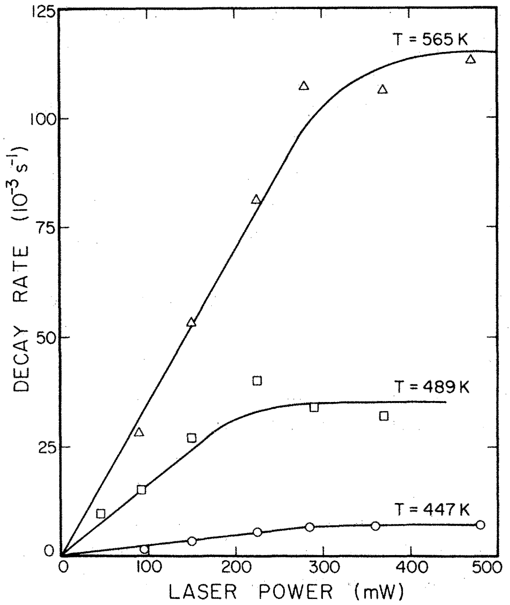

FIG. 4. Decay rates of the $(\mathrm{Zn,O})_{m=1}$ luminescence vs the laser power. For high powers the decay rates saturate due to saturation of the electron occupation of the centers. The solid lines are drawn as a guide to the eye.

The saturated decay rates are plotted versus temperature in Fig. 5. We find an activation energy of 0.60 ± 0.07 eV with a preexponential factor of approximately $3\times10^4\ \mathrm{s}^{-1}$. Similar activation energies have been observed in other GaP:(Zn,O) degradation studies.[1,3] For the data in Fig. 5 we have

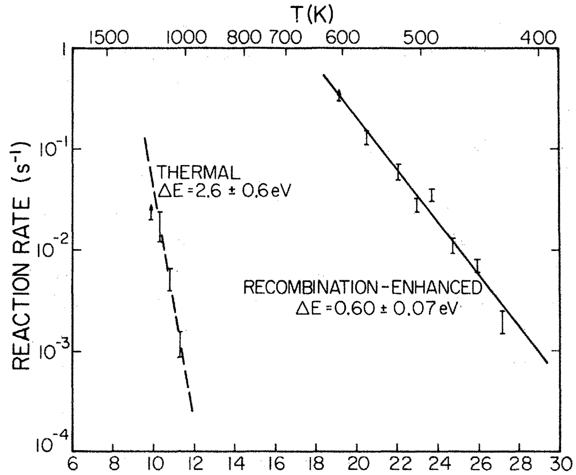

FIG. 5. Dissociation rates of $(\mathrm{Zn,O})_{m=1}$ pairs. The rates labeled "recombination-enhanced" are for photoinduced dissociation of the pairs, in the limit of high laser power. The rates labeled "thermal" are for pair dissociation by purely thermal means.

not included any corrections to the temperature due to sample heating since these corrections produce a negligible change to the activation energy within the quoted uncertainties. In addition to measuring the activation energy for the photoinduced reaction, we have also measured the barrier for the nearest-neighbor dissociation to proceed by purely thermal means. The procedure consisted of observing the absolute intensity of luminescence (at 1.77 eV) from a sample, putting it in a furnace for some amount of time, removing, quenching, and etching the sample, and finally observing again the luminescence intensity. The annealing temperatures were greater than 600 °C (the initial state of the crystal[8]) and so the luminescence intensity decreased with annealing time due to dissociation of the nearest-neighbor pairs.[7] The resulting exponential decay rates are shown in Fig. 5. The activation energy is 2.6 ± 0.6 eV with a preexponential factor of approximately 10^{10} s^{-1}. This activation energy represents the barrier for dissociation of $(\text{Zn,O})_1$ without a bound electron on the center (let us call this the ground state of the complex).

Now let us consider what mechanisms may be responsible for the photoinduced dissociation reaction. From the literature[6,22] we identify two mechanisms which have been observed in other systems. First, the $(\text{Zn,O})_1$ dissociation could be a "recombination-enhanced" defect reaction (REDR) in which energy available from electron-hole recombination is transferred to localized vibrational modes which leads to a reaction. This is the mechanism we believe to cause the reactions observed here. The activation energy of 0.60 eV we identify roughly as the difference between the thermal barrier (2.6 ± 0.6 eV) and the recombination energy (~ 1.9 eV). Since all of the recombination energy is used in surmounting the barrier, the reaction is the result of nonradiative recombination by multiphonon emission (MPE). Although MPE recombination has not been reported for $(\text{Zn,O})_1$ it has been reported[5] for isolated O and it seems likely that it also occurs for $(\text{Zn,O})_1$. The fraction of MPE recombination events which lead to a pair dissociation is estimated to be 10^{-4} (roughly, this is the value of η as defined in Ref. 6).

The second mechanism that must be considered is a "charge-state" reaction in which the $(\text{Zn,O})_1$ dissociation would occur thermally from the excited state of the complex in which the bound electron is present. At high laser powers the pairs are almost always in this state. The observed 0.60 eV would be identified as the thermal reaction barrier for this excited state. This is rather different than the ground-state barrier of 2.6 eV. A nearest-neighbor Coulomb attraction of 0.55 eV cannot completely account for this difference. Furthermore, the observed 3×10^4 s^{-1} is about 9 orders of magnitude less than a phonon frequency. This implies a multijump process in which the (Zn,O) pair dissociates and recombines 10^9 times before permanently dissociating, or in which a third particle is needed for the reaction and must diffuse to the site. Although we cannot prove that these processes are not occurring, we consider them to be unlikely and we prefer the simpler explanation of the recombination-enhanced reaction.

V. KINETICS OF ATOMIC DIFFUSION

In this section we will consider some aspects of the (Zn,O) pair dissociation and subsequent re-formation. The strong electron-phonon coupling required for a REDR is clearly evident in the $(\text{Zn,O})_1$ photoluminescence spectra.[4] This strong coupling suggests that the reaction may proceed without the presence of any additional defects. Thus, it seems quite likely that the oxygen (or zinc) simply jumps from its substitutional site to an interstitial site and migrates away. The mobile ion is subsequently captured by a vacancy to form a $(\text{Zn,O})_m$ pair with the nearest zinc (or oxygen) ion. The observed activation energy of 0.60 eV will in general contain contributions from each of the processes: dissociation, diffusion, and re-formation. From Fig. 5 it is clear that the observed reaction is a first-order kinetic process. Also, as shown in Fig. 1 the $(\text{Zn,O})_{m>1}$ pairs form at exactly the same rate as the $(\text{Zn,O})_{m=1}$ pairs dissociate. Thus, the rate limiting process is the dissociation, and the observed rates are indeed the rates for dissociation. We emphasize that it is the dissociation of the pairs which we believe to be a photoinduced reaction. The subsequent diffusion and re-formation can probably occur thermally at the temperatures considered here.

We have studied the pair re-formation process by measuring the number of pairs of a given shell number m which are produced by the aging process. Figure 6 shows low-temperature spectra in an unaged and an aged sample. The discrete lines in the spectra are $(\text{Zn,O})_m$ donor-acceptor (DA) luminescence. The broad background is due to radiative processes involving mainly recombination of electrons bound to $m=1$ and 2 pairs with holes bound to distant acceptors. The pairs responsible

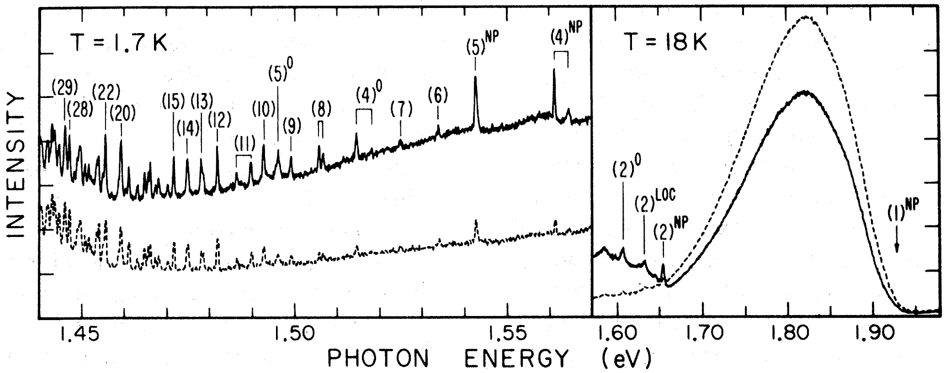

FIG. 6. Low-temperature donor-acceptor luminescence from an aged (solid line) and an unaged (dashed line) sample. The lines are labeled by m for mth-nearest-neighbor pairs with a superscript indicating the type of phonon involved in the transition (O is optical, LOC is local, NP is no-phonon). Those labels with no superscripts refer to no-phonon transitions. Note the intensity and energy scale change at 1.57 eV. The data on the left had a flat background subtracted from it.

for the discrete DA lines are labeled in accordance with previous identifications.[4,23] As discussed in Sec. III, the ratio of line intensities is equal to the ratio of pair concentrations in the samples. In the aged material, the line intensity is the sum of that from the new centers produced by the aging and that from the centers which existed prior to the aging. Thus, the concentration of centers produced by the aging is given by

$$N'_m = N_m \left[\frac{I'_m}{I_m} - 1 \right] , \qquad (12)$$

where I_m and I'_m are the luminescence intensities in the unaged and aged sample, respectively, and N_m is the pair concentration in the unaged material. N_m can be computed[24] by considering equilibrium between oppositely charged ions at the growth temperature of the crystal. For small m this is a very crude model, but it has been shown to give reasonable results.[7]

The concentration of new $m > 1$ centers produced by the aging process is dependent on the sample conditions prior to aging. Figure 7 shows typical results, based on the integrated DA line intensities of Figure 6. We see that the dissociated nearest-neighbor pairs tend to re-form as pairs with low m. The distribution of new centers contains some information about the pair re-formation process. At present we do not have a theory which allows us to uniquely identify the re-formation mechanism. In general, it appears that the mobile ion and/or the vacancy tend to stay in the vicinity of a dissociated center (i.e., an isolated Zn or O). In any case, we always observe that for $1 < m \lesssim 10$ the distribution of new centers increases sharply with decreasing m. In fact, we feel that this distribution can be extended to include $m = 1$. This extension is reasonable since we cannot think of any physical process which would allow the formation of $m > 1$ pairs while prohibiting the formation of $m = 1$ pairs. Thus, we conclude that a significant number of the dissociated $m = 1$ pairs re-form as

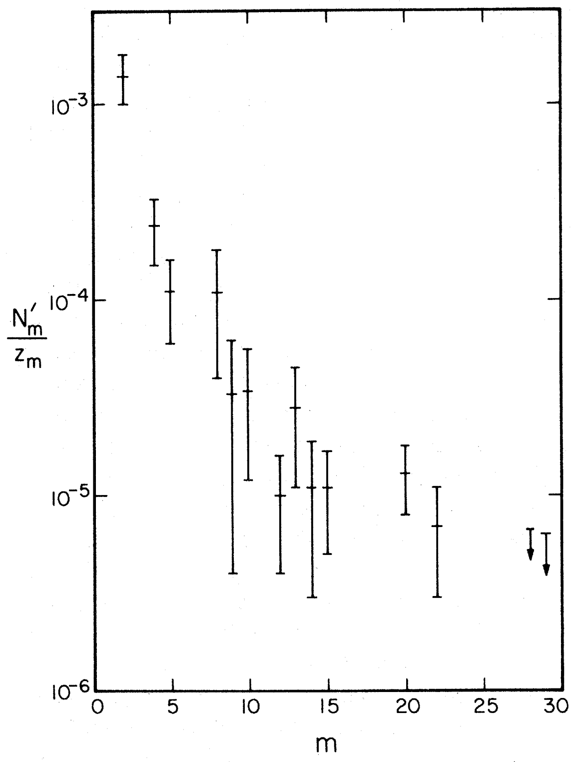

FIG. 7. The distribution of new pairs formed by the aging process. N'_m is the concentration of the mth-nearest-neighbor pairs, normalized to the total concentration of pairs (estimated) in the sample. z_m is the number of equivalent mth-nearest-neighbor sites.

other $m=1$ pairs. These pairs are subsequently dissociated and the entire aging process stops when all of the dissociated $m=1$ pairs re-form as $m>1$ pairs.

Clearly the observed aging rates will be proportional to the probability of not re-forming as a $m=1$ pair. In order to minimize the device degradation rate, the probability for $m=1$ re-formation should be maximized. This probability is dependent on the sample conditions. For example, Bergh[1] found that the presence of Cu in GaP:(Zn,O) produces an increase in the observed degradation rates. We would interpret this as being due to the formation of complexes between the dissociated, mobile ion(s) and the Cu impurity, thereby eliminating the chance of producing another $m=1$ pair. The net dissociation rate can be affected by many other similar processes. The rates of these processes must be controlled in order to produce devices with the longest lifetime.

VI. CONCLUSIONS

In this paper we have given a detailed description of photoinduced reactions between nearest-neighbor zinc and oxygen impurities in gallium phosphide. These reactions were first observed by Henry and Dapkus.[2,3] In a previous work[4] we demonstrated that the $(Zn,O)_1$ pairs were dissociating and subsequently re-forming as further separated pairs. Here, we report measurements of the dissociation rates. The observed luminescence decay curves are analyzed by a model of the electron-hole recombination kinetics which includes the effects of saturation and a spatially dependent generation rate. From the resulting dissociation rates, in the limit of high laser power, the activation energy for the photoinduced dissociation is found to be 0.60 ± 0.07 eV. We also report observations of the purely thermal dissociation of the pairs, with an activation energy of 2.6 ± 0.6 eV. From these activation energies along with the observed preexponential factors, we conclude that the dissociation is a recombination-enhanced defect reaction. A nonradiative electron-hole recombination event puts the $(Zn,O)_1$ center into a highly excited vibronic state, resulting in the dissociation. The atomic motion in the dissociation and re-formation is not well understood. However, we propose that in the dissociation the oxygen (or zinc) ion jumps to an interstitial site. This interstitial ion then diffuses thermally some short distance and is captured by a vacancy to form a pair with the nearest zinc (or oxygen) ion.

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