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Theory of recombination-enhanced defect reactions in semiconductors

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We present a quantitative theory to describe enhancement of defect reaction rates upon electron-hole recombination. The theory is based on the following mechanism: energy liberated upon nonradiative electron or hole capture is converted largely into vibrational energy that is initially localized in the vicinity of the defect. This vibrational energy can be utilized to promote defect reactions such as diffusion. The process can be described using a formulation similar to the successful Rice-Ramsperger-Kassel theory of unimolecular reactions. The resulting expression for the enhanced reaction rate depends upon two physical properties of the defect: the number of effective oscillators of the "defect molecule" and the rate of dissipation of local vibrational energy to the lattice. The theory is consistent with recent experiments of Kimerling and Lang and may be useful for understanding several related processes occurring in semiconductors.

I. INTRODUCTION

Recent experiments by Kimerling and Lang[1,2] (KL) have shown that the annealing rate at room temperature of radiation-induced defects in GaAs can be increased by a factor of about 10^6 upon introduction of a nonequilibrium concentration of minority carriers. KL established a direct connection between the resulting increased rate of electron-hole recombination at the defect and the annealing rate of a "deep" defect state with energy 0.31 eV below the conduction-band edge. See Refs. 1 and 2 for more details of this work.

These experiments give the first direct evidence for what we believe is a commonly occurring process. Nonradiative capture of an electron or hole at a deep trap is accompanied by the release of a large amount of vibrational energy around the defect. Some of this excess vibrational energy can flow into a crucial "reaction coordinate" which, when sufficiently excited, causes diffusion of the defect. Related ideas have been proposed in a different context by Seitz[3] and later by Pooley[4] and Hersh,[5] but the implications have not been fully explored. In this paper we develop a simple theory relating the rate of recombination-enhanced processes to properties of the defect and its interaction with the lattice which is consistent with the main experimental observations of KL. Our theory has some features in common with the temperature-spike model[6] but, as we shall see, the quantitative implications of the two approaches can be very different.

II. DEFECT MOLECULE

While the ideas discussed herein apply to any deep impurity or defect level, we will for the moment focus on point defects. Consider a defect which has an electronic energy level lying deep in the band gap of a semiconductor, with energy ΔE_c below the conduction band. Typically, ΔE_c is several tenths of an electron volt for a deep level (see Fig. 1). An electron which is so strongly bound will also be tightly bound, i.e., the electron will be confined to a small region of space in the vicinity of the defect. In addition, because of differences in mass or coupling to the rest of the lattice, there will typically be several localized (high-frequency or resonant) vibrational modes associated with the defect.[7,8] Thus both in its electronic and vibrational properties, the defect and its immediate neighborhood resembles a "defect molecule" imbedded in the host lattice. In what follows we will make use of concepts developed in the theory of unimolecular reactions[9] to describe possible reactions of this defect molecule construct.

III. MECHANISM OF ENERGY LOSS

In order to be captured by the defect, an electron must lose the energy ΔE_c to go from its "free" conduction-band state to a bound state localized around the defect. (Similar statements apply to hole capture.) In radiative capture this excess energy is carried off by a photon. Nonradiative capture by an Auger process (excitation of a second electron) is also possible. In this paper, however, we concentrate on a third trapping mechanism, nonradiative capture accompanied by vibrational excitation.[10]

Large electron-phonon coupling is required to make vibrational excitation the most probable capture mechanism. This strong coupling arises as a direct consequence of the localized electronic and vibrational states at the defect site.

Localized vibrational modes are characterized by large vibrational amplitudes of atoms in the vicinity of the defect. These vibrations are strongly affected by differences in local binding between the free and trapped electronic configurations. Thus these modes dominate the electron-phonon coupling terms and are favored as accepting modes for the

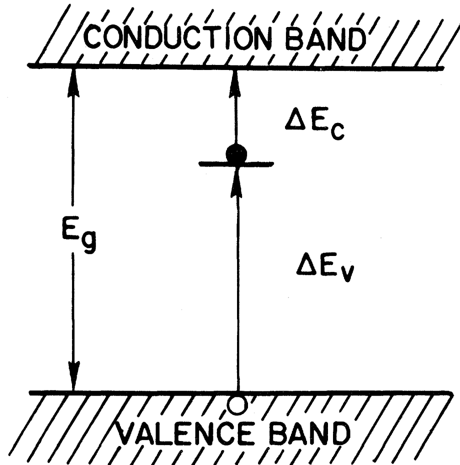

FIG. 1. Energy position of an occupied deep state with associated electron and hole transitions.

excess vibrational energy. A small fraction of the energy ΔE_c may be converted directly into delocalized lattice vibrations, particularly if trapping occurs by a cascade mechanism.[11] However none of the excited levels is likely to be bound by more than a few hundredths of an electron volt, so it is accurate to assume that most of the energy is converted into vibrations during the final step of the cascade, i.e., almost all the energy is initially deposited into the localized modes of the defect molecule.

We will not be concerned further in this paper with a theoretical treatment of the capture process, but merely make the physically plausible assumption that on nonradiative capture of an electron at a deep impurity state, a large amount of energy ΔE, essentially equal to ΔE_c, is initially deposited into local vibrations around the defect. This energy will of course eventually flow out to the rest of the lattice as thermal equilibrium is reestablished, but before it is lost it may be utilized to promote defect reactions such as diffusion. In Sec. IV we set up the rate equations which this model suggests.

IV. BASIC RATE EQUATIONS

Let $n(E)\,dE$ denote the number of defect molecules possessing internal (vibrational) energy between E and $E+dE$. By definition, $n(E)$ is zero for $E<0$. $n(E)$ can be affected by two processes. The first is thermal activation or deactivation through interaction with the rest of the lattice. This is expressed by the relation

$$n(E)\xrightarrow{r_1(E,E')}n(E')\,, \tag{1}$$

where $r_1(E,E')$ is the microscopic rate constant for this process. Equation (1) represents deactivation (loss of energy to the lattice) when $E>E'$, and thermal activation when $E<E'$. The rate constant $r_1(E,E')$ is defined so that the rate at which the internal energy of defects is changed from an initial value of E to $E+dE$ to a final value of E' to $E'+dE'$ is given by $n(E)r_1(E,E')\,dE'\,dE$. Thus $r_1(E,E')$ has units $t^{-1}E^{-1}$. A theoretical calculation of the lattice-defect interaction and hence of $r_1(E,E')$ would, of course, be very difficult.

Electron (or hole) capture can also affect the distribution $n(E)$. In this simplest version of the theory we assume that capture occurs with a rate constant R which is independent of the initial vibrational energy of the defect molecule. As discussed in Sec. III, we assume that a specified amount of energy ΔE (approximately equal to ΔE_c) is deposited into the vibrations of the defect molecule. This process is represented by the relation

$$n(E)\xrightarrow{r_3(E,E')}n(E')\,, \tag{2}$$

where

$$r_3(E,E')=R\delta(E-E'-\Delta E)\,. \tag{3}$$

The δ function in Eq. (3), which requires the energy supplied to be exactly ΔE, can be replaced by a more realistic distribution if experiments indicate this refinement is necessary.

Diffusion of the defect is treated by the following simple picture. We assume a diffusion step will occur if and only if an amount of energy greater than some specified value E^* is found in a particular "critical reaction coordinate." This critical reaction coordinate is some combination of the local vibrations around the defect molecule which when sufficiently extended results in a diffusion step.[12] We represent this picture by the reaction scheme

$$n(E)\xrightarrow{k_2(E)}n^{\neq}(E)\xrightarrow{\text{always}}\text{diffused } n(E)\,. \tag{4}$$

The symbol $\neq$ denotes an *activated* defect which always diffuses.

Here we assume there is internal flow of energy within the defect molecule (due in part to anharmonic interactions) with the rate constant $k_2(E)$ giving the rate that energy greater than the minimum amount E^* flows to the reaction coordinate. Thus $k_2(E)$ is zero for $E<E^*$ and is presumably an increasing function of energy thereafter: the higher the internal energy of the defect, the more likely that the necessary amount will find its way to the reaction coordinate. The possibility of several diffusion steps prior to deactivation by the lattice is permitted in Eq. (4) since the diffusion step does not change the energy of the defect.[13]

The total rate of diffusion steps from defects of all energies is, using Eq. (4),

$$J_d=\int_{E^*}^{\infty}k_2(E)n(E)\,dE\,. \tag{5}$$

Thus we must calculate the density $n(E)$ from Eqs. (1) and (2) and substitute this into Eq. (5). To solve these equations we invoke the familiar *steady-state hypothesis*: after an initial transient period, the number of *energized* defects (i.e., defects with energy greater than E^*) reaches a steady state.[14] That is, for $E > E^*$ we assume, using Eqs. (1)–(3),

$$\frac{d}{dt}n(E) = 0 = \int_0^\infty r_1(E', E)n(E')\,dE' - \int_0^\infty r_1(E, E')n(E)\,dE' + R\int_0^\infty n(E')\delta(E' - E + \Delta E)\,dE' - R\int_0^\infty n(E)\delta(E - E' + \Delta E)\,dE' \tag{6}$$

or

$$[k_{-1}(E) + R]n(E) = \int_0^\infty r_1(E', E)n(E')\,dE' + Rn(E - \Delta E), \tag{7}$$

where

$$k_{-1}(E) = \int_0^\infty r_1(E, E')\,dE' . \tag{8}$$

Here $k_{-1}(E)$ is the total rate of energy exchange between defect molecules of energy E and the lattice. The first two terms in Eq. (6) refer to population and depopulation of defects of energy E by (thermal) interactions with the lattice. The third and fourth terms similarly refer to the recombination process. The recombination rate R is typically many orders of magnitude smaller than the thermal energy transfer rate $k_{-1}(E)$, so we neglect R on the left-hand side of Eq. (7).

Combining Eqs. (7) and (5) we have

$$J_d = \int_{E^*}^\infty \frac{k_2(E)}{k_{-1}(E)}\left(\int_0^\infty r_1(E', E)n(E')\,dE' + Rn(E - \Delta E)\right)dE . \tag{9}$$

We now make a further *quasiequilibrium assumption*. We assume that recombination events are sufficiently rare that it is accurate to replace the distribution $n(E)$ in the integral of Eq. (9) by the thermal equilibrium value $n_{eq}(E)$. This is a good approximation since the recombination process produces only a minor fractional change in $n(E)$ for energies less than E^* and it is these values of $n(E)$ which make the major contribution to the integral in Eq. (9).

We define the thermal equilibrium fraction of defects $f(E)\,dE$ with energy between E and $E + dE$ as

$$f(E) = n_{eq}(E)/N, \tag{10}$$

where N is the total number of defects. But since thermal equilibrium is established by process (1), detailed balance requires that

$$\int_0^\infty r_1(E', E)n_{eq}(E')\,dE' = \int_0^\infty r_1(E, E')n_{eq}(E)\,dE' = k_{-1}(E)Nf(E) . \tag{11}$$

Thus, substitution of $n_{eq}(E)$ for $n(E)$ in Eq. (9) gives $J_d = Nk_d$, where the diffusion rate constant is given by

$$k_d = \int_{E^*}^\infty k_2(E)\left(f(E) + \frac{Rf(E - \Delta E)}{k_{-1}(E)}\right)dE . \tag{12}$$

Hence the diffusion rate constant is the sum of two terms:

$$k_d = k_d(\text{thermal}) + k_d(\text{enhanced}), \tag{13}$$

where

$$k_d(\text{thermal}) = \int_{E^*}^\infty k_2(E)f(E)\,dE \tag{14}$$

and

$$k_d(\text{enhanced}) = R\int_{E^*}^\infty \frac{k_2(E)}{k_{-1}(E)}f(E - \Delta E)\,dE . \tag{15}$$

k_d(thermal) is the diffusion rate from ordinary thermal processes and k_d(enhanced) is the extra diffusion caused by the capture process.

V. RICE-RAMSPERGER-KASSEL THEORY

We can get approximate values for the factors $k_2(E)$ and $f(E)$ from the familiar RRK (Rice-Ramsperger-Kassel) theory of unmolecular reactions.[15] The RRK model assumes that the defect molecule is made up of S loosely coupled oscillators, all having the same vibrational frequency. If the lattice is at a temperature T, each degree of freedom of the defect molecule will have a Boltzman distribution of energy. The equilibrium fraction of such defects having a total energy E (which of course can be distributed in any way among the S degrees of freedom of the defect), can be obtained by a simple calculation[9]:

$$f(E)\,dE = \frac{1}{(S-1)!}\left(\frac{E}{kT}\right)^{S-1}\frac{1}{kT}\,e^{-E/kT}\,dE . \tag{16}$$

Note that the fraction of energized defects is greater for a complex defect with many degrees of freedom than for a simple defect with only one degree of freedom, to which the ordinary Boltzman distribution applies.

The RRK model further assumes that there is a flow of energy among the modes of the defect molecule (due in part to anharmonic forces) so that a statistical distribution of energy among the modes is rapidly established. The rate that the required energy E^* will flow into a particular critical mode when the defect molecule has a total energy E is taken to be proportional to the probability that in a random distribution of the total energy E among all the modes, a particular one will have an energy E^*. This again is a standard statistical problem and an approximate (classical) result is[9]

$$k_2(E) = k^{\neq}\left(\frac{E-E^*}{E}\right)^{S-1}, \tag{17}$$

where $k^{\neq}$, the proportionality constant corresponding to the maximum rate of energy flow, is presumably of the order of a vibrational frequency.

The RRK results, Eqs. (16) and (17), are based on an oversimplified model. However they do take into account three essential physical features that must be present in any more exact expressions: (a) The greater the number of degrees of freedom S of the defect, the greater will be the equilibrium fraction of energized defects. (b) For a given total defect energy, the greater the number of degrees of freedom, the smaller will be the probability that the critical amount appears in a single mode. (c) For a given number of degrees of freedom, the greater the total energy, the more rapidly will the critical mode attain the amount required to achieve diffusion.

The RRK theory has proved qualitatively successful in fitting experimental data on unmolecular decomposition, where the effective number of oscillators S is taken as an empirical parameter. Furthermore, the assumption of rapid energy flow between modes has been verified experimentally for molecules in almost all cases.[9] If information about the distribution of vibrational (and internal rotational) frequencies of the molecule is available, then a quantitative version of the theory with no adjustable parameters can be applied (the RRKM theory).[16] In this simplest approach we have used the RRK model since we know very little about the nature of the defects. As more becomes known, improved expressions for $k_2(E)$ and $f(E)$ can be derived, but the qualitative success of the simple RRK theory for unimolecular reactions gives us hope that it will also prove useful for defect reactions.

VI. APPROXIMATE EVALUATION OF THE DIFFUSION RATE

Substituting the RRK results, Eqs. (16) and (17) into Eqs. (14) and (15) we have, first for the ordinary thermal term,

$$k_d(\text{thermal}) = k^{\neq}\int_{E^*}^{\infty}\left(\frac{E-E^*}{E}\right)^{S-1}\frac{1}{(S-1)!}\left(\frac{E}{kT}\right)^{S-1} \times \frac{1}{kT}\,e^{-E/kT}\,dE = k^{\neq}e^{-E^*/kT}. \tag{18}$$

Thus the RRK theory gives the familiar Arrhenius form for the ordinary (thermal) diffusion rate constant and we can identify E^* as the activation energy for diffusion and $k^{\neq}$ as the prefactor.

The expression for the enhanced diffusion rate is more complicated:

$$k_d(\text{enhanced}) = R\int_{E^*}^{\infty}\frac{k^{\neq}}{k_{-1}(E)}\left(\frac{E-E^*}{E}\right)^{S-1}\frac{1}{(S-1)!} \times \left(\frac{E-\Delta E}{kT}\right)^{S-1}\frac{1}{kT}\,e^{-(E-\Delta E)/kT}\,dE\,. \tag{19}$$

[The lower limit of the integral in Eq. (19) should be ΔE rather than E^* if $\Delta E > E^*$.] This expression involves $k_{-1}(E)$, the total rate of energy exchange between a defect molecule of energy E and the lattice. Since $k_{-1}(E)$ can be expected to be a slowly varying function of E, we approximate it by some average value, denoted $k_{-1}(\bar{E})$.

We consider the usual situation where the activation barrier E^* is large compared to the average thermal energy of the defect molecule. That is

$$E^* \gg (S-1)\,kT\,. \tag{20}$$

We first assume that the energy supplied on capture, ΔE, is no greater than E^*, i.e.,

$$E^* \geqslant \Delta E\,. \tag{21}$$

Letting $X=(E-E^*)/kT$, $X^*=E^*/kT$, and $\Delta X = \Delta E/kT$, Eq. (19) becomes

$$k_d(\text{enhanced}) = R\,\frac{k^{\neq}}{k_{-1}(\bar{E})}\,e^{-(X^*-\Delta X)} \times \int_0^{\infty}dX\left\{\frac{X^{S-1}}{(S-1)!}\,e^{-X}\right\}\left(\frac{X+X^*-\Delta X}{X+X^*}\right)^{S-1}. \tag{22}$$

The term in curly brackets in the integrand of Eq. (22) has its maximum value at $X = S-1$ and falls to zero rapidly thereafter. Thus we can ignore X in the denominator of the slowly varying term $[(X+X^*-\Delta X)/(X+X^*)]^{S-1}$, using Eq. (20). Equation (22) can then be integrated by parts exactly. The result is particularly simple in two limits.

The first limit, which we will later apply to interpret the experiments of KL, arises when

$$E^* - \Delta E \gg (S-1)\,kT\,. \tag{23}$$

Then we can ignore X in the numerator as well as the denominator of the slowly varying term in Eq. (22) and get the simple result

$$k_d(\text{enhanced}) \cong R\,\frac{k^{\neq}}{k_{-1}(\bar{E})}\left(\frac{E^*-\Delta E}{E^*}\right)^{S-1}e^{-(E^*-\Delta E)/kT}. \tag{24}$$

Thus the enhanced diffusion rate is directly proportional to the rate of capture R. There is an "efficiency factor" $[(E^*-\Delta E)/E^*]^{S-1}$ in the prefactor relating to the probability that the energy distributed among the S modes can find its way to the critical diffusive mode; when S is large this probability becomes small. The factor $k^{\neq}/k_{-1}(\bar{E})$ is the ratio of the rate of internal equilibrium within the defect molecule to the rate of equilibration with the lattice. If the defect has several strongly localized vibrational modes, one might expect the rate of internal equilibration to be significantly faster than

the rate of energy loss to the lattice, while the ratio could be near unity for defects which cause relatively small vibrational perturbations.

The activation energy for the enhanced process is reduced from that of the thermal process by ΔE, the amount of energy supplied to the defect on capture. It is this reduction that gives the possibility of greatly increased diffusion rates.

Another limit in which simple results are found from Eq. (23) arises when $E^* - \Delta E \ll (S-1)kT$. Then

$$k_d(\text{enhanced}) \cong R \frac{k^{\neq}}{k_{-1}(\overline{E})} \frac{(2S-2)!}{(S-1)!} \left(\frac{E^*}{kT}\right)^{1-S} e^{-(E^*-\Delta E)/kT} . \tag{25}$$

Thus if E^* approaches ΔE, the activation energy for the enhanced-diffusion process tends to zero (apart from any contained in the recombination rate R). In this limit the diffusion is essentially *athermal*.

If $\Delta E > E^*$, as may be the case for some defects in wide band-gap materials, there is again no apparent activation energy for the enhanced process. If $\Delta E - E^* \ll (S-1)kT$, we find as in Eq. (25)

$$k_d(\text{enhanced}) \cong R \frac{k^{\neq}}{k_{-1}(\overline{E})} \frac{(2S-2)!}{(S-1)!} \left(\frac{E^*}{kT}\right)^{1-S} . \tag{26}$$

Another simple limit arises when $\Delta E - E^* \gg (S-1)kT$. We find from Eq. (19) in this case

$$k_d(\text{enhanced}) = R \frac{k^{\neq}}{k_{-1}(\overline{E})} \left(\frac{\Delta E - E^*}{\Delta E}\right)^{S-1} . \tag{27}$$

In the intermediate cases or when Eq. (20) no longer holds, one can easily numerically integrate Eq. (19).

VII. COMPARISON WITH EXPERIMENT

KL measured both the thermal and the recombination-enhanced annealing rate of a defect state located 0.31 eV below the conduction band in GaAs.[1,2] They found the thermal annealing rate of this defect to be of the form

$$k_a(\text{thermal}) = K_t e^{-E_t^*/kT} , \tag{28}$$

where $K_t \cong 10^{11}$ sec^{-1} and $E_t^* = 1.4 \pm 0.15$ eV. After injection they measured a recombination-enhanced annealing rate of the form

$$k_a(\text{enhanced}) = K_e e^{-E_e/kT} , \tag{29}$$

where $K_e \cong 25$ sec^{-1} and $E_e = 0.34$ eV. They also experimentally measured the electron-hole recombination rate R and found the form

$$R = R_0 e^{-E_R/kT} , \tag{30}$$

with $R_0 = 5\times 10^8$ sec^{-1} and $E_R = 0.1$ eV. We will show that these experimental results are consistent with the predicted enhanced diffusion rate in Eq. (24).

If N_j is the average number of diffusion steps a defect must take to reach a sink and be annealed, then the annealing rate k_a is simply related to the diffusion step rate previously calculated in Eqs. (24) and (18) by

$$k_a = k_d / N_j . \tag{31}$$

The defects act as recombination centers, i.e., after a minority carrier (a hole in this case) is captured and before it can be thermally ejected, a majority carrier (electron) is captured and recombination takes place, bringing the defect back to its original state. In principle both electron and hole capture will result in enhanced diffusion, but the measured diffusion rate will be dominated by the capture process releasing the most energy to the defect.

In this case the electron capture gives about $\Delta E_c = 0.31$ eV and since the band gap in GaAs is 1.4 eV, the hole capture gives about $\Delta E_v = 1.09$ eV (see Fig. 1). Thus the hole capture rate (i.e., the recombination rate) and the hole energy will dominate the enhanced diffusion rate. Here we have assumed that the time between capture events is long enough that a defect capturing a carrier will have lost most of the local energy to the lattice before the oppositely charged carrier can be captured. This is a good approximation since the recombination rate is $\cong 10^8$ sec^{-1} which is several orders of magnitude less than a typical relaxation rate (10^{11}–10^{13} sec^{-1}).

The theoretical thermal annealing rate given in Eqs. (18) and (31) is easily related to the measured rate in Eq. (28). Thus the experimental prefactor K_t is $K_t = k^{\neq}/N_j$ and the experimental activation energy $E_t^* = E^*$. We will use these experimentally measured values in checking the predicted enhanced annealing rate, given from Eq. (31), (30), and (24) as

$$k_a(\text{enhanced}) = R_0 e^{-E_R/kT} \left(\frac{k^{\neq}/N_j}{k_{-1}(\overline{E})}\right) \left(\frac{E^* - \Delta E}{E^*}\right)^{S-1} \times e^{-(E^*-\Delta E)/kT} . \tag{32}$$

Equation (32) shows that the experimental enhanced activation energy E_e should be given by

$$E_e = E^* - \Delta E + E_R . \tag{33}$$

Assuming $\Delta E \cong \Delta E_v = 1.09$ eV for hole capture and using experimental values for E^* from Eq. (28) and E_R from Eq. (30) we have

$$E_e = (1.4 \pm 0.15) - 1.09 + 0.1 = (0.41 \pm 0.15) \text{ eV}. \tag{34}$$

As previously noted by KL,[2] this agrees with the experimental result $E_e = 0.34$ eV from Eq. (29).

The predicted prefactor is of the form

$$K_e = R_0 \left(\frac{k^{\neq}/N_j}{k_{-1}(E^*)}\right) \left(\frac{E^* - \Delta E}{E^*}\right)^{S-1} \tag{35}$$

$$= 5\times10^{8}\left(\frac{10^{11}}{k_{-1}(\overline{E})}\right)(0.17)^{S-1}, \qquad (36)$$

where we have used Eq. (33) to give us $E^* - \Delta E = E_e + E_R$ and Eqs. (28) and (30). Equation (36) has two unknown quantities: S, the number of effective oscillators in the defect molecule, and k_{-1}, the average rate of equilibration with the lattice. We are able to fit the experimental value for K_e (=25 $\sec^{-1}$) with reasonable values for each parameter. Thus if $k_{-1} = 10^{13}$ $\sec^{-1}$, which implies rapid equilibration, then $S=8$ fits the data. If k_{-1} is 10^{11} $\sec^{-1}$, then $S=10$ fits the data. The number of effective oscillators S is not very sensitive to the choice of k_{-1} and the predicted values are reasonable estimates for the number of localized modes around a point defect. The theory thus seems internally consistent and able to fit the available experimental data of KL.

Further confirmation for the model described here comes from very recent experimental studies of Kimerling and Lang[17] on the annealing of point defects in GaP. Here the band gap (~2.2 eV) is much larger than it is in GaAs and ΔE appears to be greater than E^*. Precise values for these parameters are not yet available, but the recombination-enhanced process proceeds athermally, in agreement with the predictions of Eq. (27).

VIII. DISCUSSION

We discuss now some qualitative implications of the present theory. These topics will be treated in detail in a future paper. Two main points are considered: (a) possible contributions of electron-hole recombination to reactions at thermal equilibrium and (b) materials parameters which maximize recombination-enhancement effects under conditions of outside stimulation.

Under equilibrium conditions carriers are continually excited from and captured at the defect. It is conceivable, therefore, that these electronic transitions could provide an enhancement of reaction rates even in the absence of outside stimulation; i.e., k_D(enhanced) might be the dominant term in Eq. (13) even under equilibrium conditions. However, in this case there will be no lowering of the activation barrier in the enhanced diffusion term because at equilibrium, the creation of the carriers is itself a thermally activated process. Furthermore, the prefactor in k_d(enhanced) is usually several orders of magnitude smaller than typical values (10^{11}–10^{13} $\sec^{-1}$) for the prefactor in the term k_a (thermal). Thus recombination enhancement is not thought to be an important process under equilibrium conditions.

When a nonequilibrium distribution of electrons and holes is established, the following factors will determine the importance of recombination enhancement. First, the defect must be a good recombination center, accommodate nonradiative electronic transitions, and, hence, possess strong electron-phonon coupling. Thus most examples should be found in more ionic semiconductors. Second, the energy involved in the electronic transition must be significant relative to the reaction barrier. Thus, large band-gap materials are favored. Finally, the recombination rate must be high relative to the thermal excitation rate. Thus, high injection levels and high majority carrier concentrations are preferred.

IX. CONCLUSIONS

We have developed a theory of recombination-enhanced defect reactions based on the hypothesis that vibrational energy liberated upon electron or hole capture can be utilized to promote reaction. The theory considers explicitly the consequences of distributing a fixed amount of energy among a small number of oscillators that are coupled to each other and to the rest of the lattice.

An alternative approach would be to picture the energy deposition process in terms of a local heating of the lattice, i.e., a thermal spike. However, it is difficult to define a statistical parameter such as temperature within the small ensemble of oscillators composing a point defect. Furthermore, it can be estimated from the thermal-spike theory of Seitz[6] that for clusters containing less than about 20 atoms, energy loss to the lattice will occur too rapidly for a Boltzmann distribution to be established. In those cases where the temperature-spike theory is appropriate (i.e., when the defect molecule possesses a large number of vibrational modes), the two theories become equivalent. However, the present theory is valid under much more general conditions. It is likely that in most real situations the present theory will be valid, whereas the temperature spike model will not.

A fundamental result of the present theory is that the reaction rate constant is the sum of two terms, the usual thermally activated rate plus an additional term directly proportional to the recombination rate. The basic equations, (13)–(15), can be evaluated using approximations analogous to those of the RRK theory of unimolecular reaction. This analysis results in a simple analytic expression for the enhanced rate, containing an apparent activation energy lowered by the amount of vibrational energy supplied during capture. If sufficient information were known about the defect, then the theory could in principle be made quantitative, with no adjustable parameters, in analogy to the successful RRKM theory of unimolecular reactions.

Even in the semiquantitative RRK form presented here, the theory should be quite useful. The ex-

pression for the enhanced reaction rate involves two parameters: the number of effective oscillators S of the defect molecule and the ratio $k^{\ne}/k_{-1}$ of the rates of redistribution of energy within the defect molecule to exchange of energy with the lattice. With reasonable values for these parameters, the theory accurately reproduces the observations of KL on recombination enhanced annealing in GaAs. We are hopeful that similar agreement can be achieved with a great many other experimental measurements. In addition, because the parameters are directly related to physical properties of the defect and its environs, the theory should be useful in suggesting trends and in understanding the qualitative behavior of many different systems.

The most important feature of any successful theory, of course, is that it incorporate the correct physics of the situation. We feel strongly that the mechanism underlying the present theory, promotion of reaction by vibrational energy liberated upon electron or hole capture, is the one responsible for the observations of KL.

This phenomenon suggests a primary mechanism for the well known tendency of injection-mode semiconductor devices (tunnel diodes,[18] laser diodes,[19] and electroluminescent diodes[20]) to degrade under operation. In addition, recombination enhancement may be active in semiconductor materials and devices exposed to ionizing radiation and particle bombardment.[21] We believe that correlation of degradation or defect reaction kinetics with the level of outside stimulation within the framework of the above theory may provide a key to the understanding of these anomalous phenomena.

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[9]See, for example, (a) P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, London, 1972); and (b) K. J. Laidler, *Theories of Chemical Reaction Rates* (McGraw-Hill, New York, 1969).

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[14]See, for example, H. S. Johnson, *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966), p. 329ff.

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