

Nonradiative multiphonon capture of free carriers by deep-level defects in semiconductors: Adiabatic and nonadiabatic limits

H. Sumi

Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

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The rate of multiphonon capture with thermally activated temperature dependence is formulated with the semiclassical approximation for phonons. It bridges the nonadiabatic (weak-coupling) and the adiabatic (strong-coupling) limits when the interaction to induce capture is strengthened. Except in the nonadiabatic limit it is important that once-captured carriers can be reemitted into free states in a very short time (much shorter than an average phonon period) after capture. In the adiabatic limit, the preexponential factor σ_∞ of the capture cross section, being proportional to T^{-2} at a temperature T , reaches a maximum of the order of 10^{-14} cm², while that of the carrier-emission rate reaches a constant of the order of an average phonon frequency. Moreover, in this limit σ_∞ does not include defect parameters any more and depends only on the effective mass of free carriers. These features of the adiabatic limit explain well Henry and Lang's observation that σ_∞ being of the order of 10^{-14} – 10^{-15} cm² is apparently a universal quantity independent of defects within GaAs and GaP. The strength of the interaction is determined by the bandwidth of free carriers for defects with only one bound state, and a parameter distinguishing between the adiabatic and the nonadiabatic limits is given.

I. INTRODUCTION

Much interest has recently been aroused in dynamic multiphonon processes taking place around a deep-level defect in semiconductors in both basic and applied research: Free carriers injected into semiconductors are nonradiatively captured by defects into a level located deeply in a forbidden gap, and they recombine nonradiatively there.^{1,2} Therefore deep-level defects affect efficiencies of injection-mode devices such as light-emitting and laser diodes. During the capture or recombination processes an excess electronic energy of the order of a forbidden-gap one is dissipated by multiphonon emission because of a strong electron-phonon interaction in a deep level.³ Moreover, it has been observed that many phonons emitted around a defect upon capture or recombination greatly enhance movement of the defect itself or production of a new one around it.^{4–6} Therefore, it plays a decisive role in degradation of injection-mode devices, whose reliability is one of the main current interests in optoelectronics.^{7,8} Moreover, a possibility was pointed out^{9,10} that phonons emitted upon capture of an injected minority carrier induce subsequent capture of a majority carrier by the same defect; hence, an injected minority carrier recombines in a very short time of the order of a phonon period (~ 0.1 psec) after its capture. In this case a deep-level defect can be regarded as providing a tunnel through the for-

bidden gap for nonradiative recombination.

Semiconductors, such as GaAs, $\text{Ga}_{1-x}\text{Al}_x\text{As}$, $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, GaP, and $\text{GaAs}_x\text{P}_{1-x}$, used for injection-mode optical devices have a wide energy band for free carriers whose width amounts to about several electron volts. Therefore electron motion is very fast compared with phonon motion therein. Then it is reasonable to expect that the process of nonradiative multiphonon capture of an injected minority carrier can adequately be described as a situation close to the adiabatic limit, rather than close to the opposite nonadiabatic limit. Many theories^{3,11–14} have already been presented so far on the rate of multiphonon capture, with the use of various methods. But it was recently shown^{15–17} that the previous results are essentially the same as obtained by the perturbational expansion second order in an interaction between the free and the deep electronic states. The second-order perturbational treatment can be justified only in the nonadiabatic (weak-coupling) limit.¹⁸ The capture rate has not been calculated in the adiabatic (strong-coupling) limit which seems more important in usual semiconductors. The present work is devoted to giving an expression of the capture rate which bridges the nonadiabatic and the adiabatic limits. (The brief report can be found in Ref. 19.)

Adiabaticity in the capture process manifests itself in that after capturing a carrier a defect reemits it into free states in a very short time if the interac-

tion between the free and the deep states is strong enough. The effect of reemission was first taken into account by Henry and Lang.³ But their treatment is too approximated to describe correctly the adiabatic limit. In fact, the capture rate obtained by them approaches zero, after reaching a maximum, as the interaction strength is increased toward the adiabatic limit.^{5,20} On the other hand, the present work will show that toward the adiabatic limit the capture rate should show saturation, approaching a constant which does not include the interaction strength any more.

The capture cross section σ has traditionally been used for the analysis of experimental data, and it shows a temperature dependence of a thermally activated type as

$$\sigma = \sigma_{\infty} \exp(-E_A/k_B T) \quad (1.1)$$

at high enough temperatures T in the case of nonradiative multiphonon capture investigated here. Henry and Lang³ observed an important fact² that the preexponential factor σ_{∞} being of the order of 10^{-15} – 10^{-14} cm² is apparently a universal quantity for various deep-level defects within GaAs and GaP. They tried to reproduce the observed magnitude of σ_{∞} theoretically, but their heuristic model estimating the interaction to induce capture was open to criticism.¹⁶ The present work will show that the maximum value of σ_{∞} obtained in the adiabatic limit, although proportional to T^{-2} , depends only on the effective mass of free carriers, independently of various species of defects, and it is of the order of 10^{-14} cm² in GaAs and GaP. Therefore, Henry and Lang's observation seems obtainable simply as a result of the fact that the electron-phonon interaction can adequately be treated adiabatically in GaAs and GaP with a wide energy band.

Except in the adiabatic limit the capture rate depends on the strength of the interaction between the free and the deep states. Various models^{3,11–14,21,22} have been presented for the interaction strength, depending on different models for the defect potential and the wave function of an electron trapped by it. They give different values of the capture rate. The present work will show that the interaction strength can be determined by only three parameters, the depth and the lattice-relaxation energy of the deep state and the energy bandwidth of free carriers, so long as the defect has only one bound state. Therefore the result can easily be applied to the analysis of experimental data.

The adiabatic and the nonadiabatic limits are explained in Sec. II, and it will be shown that the capture rate in the adiabatic limit can be determined irrespective of the strength of the interaction to in-

duce capture so long as it is strong enough. The interaction strength is obtained in Sec. III. The capture rate bridging the two limits is calculated in Sec. IV with the use of the diagram expansion of the density matrix with the semiclassical treatment of the electron-phonon interaction. It will be shown that reemission of carriers just after capture can be described by the Landau-Zener formula^{23,24} which was originally proposed for the atomic collision of the second kind incorporating an electron transfer between colliding atoms. Discussion is left to Sec. V.

II. ADIABATIC AND NONADIABATIC LIMITS

For simplifying terminologies, we consider the case that electrons in a conduction band are captured by a defect. The electron-phonon interaction in the host lattice is neglected in comparison with that in the localized deep state. Then the Hamiltonian of the host lattice can be written as $H_F + H_L$, where H_F describes free electrons and H_L phonons. We write H_L in a usual form,

$$H_L = \sum_j \hbar \omega_j (b_j^\dagger b_j + \frac{1}{2}), \quad (2.1)$$

where b_j represents the annihilation operator for a phonon of the j th normal mode with energy $\hbar \omega_j$. The presence of a deep-level defect gives rise to a defect potential $V_d(r)$ for an electron with a coordinate r when the surrounding lattice is not distorted, and the potential is increased by $-g_d(r)Q$ when it is distorted, where Q defined by

$$Q = \sum_j V_j (b_j + b_j^\dagger) \quad (2.2)$$

represents a configuration coordinate describing the distortion. Here coefficient V_j is regarded as a real number without losing generality. Then the total Hamiltonian is given by

$$H = H(Q) + H_L, \quad (2.3)$$

with

$$H(Q) = H_F + V_d(r) - g_d(r)Q. \quad (2.4)$$

When the defect captures an electron, the surrounding lattice relaxes because of $-g_d(r)Q$ in (2.4) representing the electron-phonon interaction in the deep state. Let us describe the configuration of the relaxed lattice by $Q = Q_d$. The electronic part $H(Q)$ of the total Hamiltonian is diagonalized at $Q = Q_d$, as

$$H(Q_d) = \sum_f E_f a_f^\dagger a_f - \Delta a_d^\dagger a_d, \quad (2.5)$$

where a_f represents the operator annihilating an

electron at the f th free state with energy E_f (≥ 0) and a_d at the deep state whose energy is lower by Δ than the lowest edge of the free states at the relaxed lattice configuration. It was assumed in (2.5) that the defect provides only one bound state. Note that Δ represents the threshold energy for optical excitation of an electron trapped in the deep state to the free states under the semiclassical Franck-Condon principle. Note, moreover, that wave functions $|f\rangle$ and $|d\rangle$ of the free and the deep states, respectively, do not include the phonon coordinate Q as a parameter. The situation is quite different from the usual Born-Oppenheimer adiabatic-coupling scheme. The procedure adopted here has been called the static-coupling scheme,^{25,26} and it is more transparent for the present purpose, as discussed in Sec. V.

The electronic part $H(Q)$ of the total Hamiltonian can be rewritten as $H(Q_d) + g_d(r)(Q_d - Q)$ with $H(Q_d)$ given by (2.5), where $g_d(r)(Q_d - Q)$ gives rise to an interaction between the free and the deep states. Note here that $g_d(r)$ is large only in the neighborhood of the defect in the whole crystal with volume V . Then $\langle f | g_d(r) | f' \rangle$ is of the order of V^{-1} while $\langle f | g_d(r) | d \rangle$ and $\langle d | g_d(r) | d \rangle$ are, respectively, of the order of $V^{-1/2}$ and V^0 . We neglect $\langle f | g_d(r) | f' \rangle$ consistently with the approximation that we neglected phonon effects on the free states. We can set $\langle d | g_d(r) | d \rangle$ to be unity without losing generality [readjusting V_j to $\langle d | g_d(r) | d \rangle V_j$ in (2.2)]. In this case Q gets a dimension of energy. Then the phonon Hamiltonian associated with the deep state is given by $-\Delta + Q_d - Q + H_L$, which is rewritten as

$$\sum_j \hbar \omega_j \left[\left(b_j^\dagger - \frac{V_j}{\hbar \omega_j} \right) \left(b_j - \frac{V_j}{\hbar \omega_j} \right) + \frac{1}{2} \right] - S - \Delta + Q_d,$$

with

$$S = \sum_j V_j^2 / \hbar \omega_j. \quad (2.6)$$

Here S represents the lattice-relaxation energy at the relaxed deep state with a configuration determined by $b_j + b_j^\dagger = 2V_j / \hbar \omega_j$, at which (2.2) gives $Q_d = 2S$. On the other hand, the phonon Hamiltonian associated with the f th free state is given by $E_f + H_L$. When $E_f + H_L$ and $H_L - Q - \Delta + Q_d$ are written along a coordinate Q in the multidimensional configuration coordinate space, they give adiabatic potentials written, respectively, as

$$V_f(Q) = E_f + \frac{1}{4} Q^2 / S \quad (2.7)$$

and

$$V_d(Q) = \frac{1}{4} (Q - 2S)^2 / S - E_d, \quad (2.8)$$

with

$$E_d = \Delta - S, \quad (2.9)$$

where E_d represents the thermal depth of the relaxed deep state, which is smaller by S than the optical depth Δ because of the lattice relaxation. The energy of the deep state at the unrelaxed lattice configuration $Q=0$ is given by $V_d(0) \equiv V_d$, as

$$V_d = S - E_d = 2S - \Delta. \quad (2.10)$$

Coordinate Q in (2.7) and (2.8) has often been called the interaction-mode coordinate²⁷ in solid state physics or the reaction coordinate²⁸ in chemistry. Figure 1 shows $V_d(Q)$ and $V_f(Q)$ for various f 's as a function of Q , where case (I) for $S < \frac{1}{2}\Delta$ and case (II) for $S > \frac{1}{2}\Delta$ are distinguished with respect to relative positions of $V_d(Q)$ and $V_f(Q)$. Case (II) for strong electron-phonon coupling seems realized by a defect giving rise to the persistent photoconductivity.²⁹

Transitions between the free and the deep states are induced by

$$t_{fd} \equiv (Q_d - Q) \langle f | g_d(r) | d \rangle. \quad (2.11)$$

Then the electronic part of the total Hamiltonian is written as

$$H(Q) = H_0(Q) + H', \quad (2.12)$$

with

$$H_0(Q) = \sum_f E_f a_f^\dagger a_f + (V_d - Q) a_d^\dagger a_d \quad (2.13)$$

and

$$H' = \sum_f (t_{fd} a_f^\dagger a_d + t_{fd}^* a_d^\dagger a_f). \quad (2.14)$$

In the process of capture of an electron by a defect, electrons are initially populated with the thermal-equilibrium distribution in the adiabatic potentials $V_f(Q)$ for various f 's shown in Fig. 1. They eventually make a transition to the states of the adiabatic potential $V_d(Q)$ and are captured by the defect. At low temperatures where $k_B T$ is much smaller than an average phonon energy $\hbar \bar{\omega}$, an electron tunnels a potential barrier from the bottom of $V_f(Q)$ to $V_d(Q)$ horizontally in Fig. 1. It is important in this case to note that nuclear tunneling as well as electron tunneling occurs between different Q 's, and that the capture rate should be independent of temperature.³⁰ At high temperatures for $k_B T \gg \hbar \bar{\omega}$, on the other hand, nuclear tunneling does not occur, and transitions take place at the crossing point between $V_f(Q)$ and $V_d(Q)$ conserving Q .³⁰ We get from (2.7)–(2.9) that $V_f(Q)$ for $E_f = 0$ crosses with $V_d(Q)$ at $Q = V_d$ and $V_f(V_d) - V_f(0)$ equals $\frac{1}{4}(\Delta - 2S)^2 / S$. Then the capture rate should show a temperature dependence of a thermally ac-

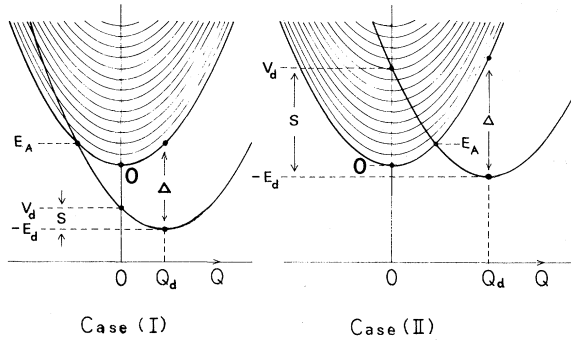


FIG. 1. Adiabatic potential for the bottom of the free states, above which there exists a continuum of them shown by thin solid lines, and that for the deep state isolated from the continuum. They are shown as a function of the configuration coordinate Q describing capture of a free electron into the deep state. Energy E_A represents the thermal-activation energy of capture, and S , E_d , and Δ represent, respectively, the lattice-relaxation energy and the thermal and the optical depths of the deep state. The left-hand side shows case (I) for $2S < \Delta$, while the right-hand side shows case (II) for $2S > \Delta$.

tivated type dominated by $\exp(-E_A/k_B T)$ with

$$E_A = \frac{1}{4}(\Delta - 2S)^2/S. \quad (2.15)$$

The present work treats only this high-temperature semiclassical case which is sufficient in order to analyze various phenomena taking place in injection-mode devices under operation, although the result can easily be extended to the temperature region of $k_B T \gtrsim \hbar\omega$ as discussed in Sec. V.

An electron occupying the f th free state makes a transition to the deep state at $Q = V_d - E_f$, where $V_f(Q) = V_d(Q)$, and the electron is captured by the defect when the surrounding lattice relaxes from $Q = V_d - E_f$ to $Q = Q_d (= 2S)$ along $V_d(Q)$. However, it is apparent from Fig. 1 that $Q = V_d - E_f$ is located on the higher-energy side along $V_d(Q)$ than $Q = V_d$, where $V_d(Q)$ crosses with the lowest curve of $V_f(Q)$ for $E_f = 0$. Therefore, in the course of relaxation of Q from $V_d - E_f$ to Q_d along $V_d(Q)$, the deep state is embedded in the continuum of free states in the initial time region of $V_d - E_f < Q < V_d$. It is in this time region that the electron once captured in the deep state can be reemitted into free states. The nonadiabatic limit corresponds to a case where the reemission probability of a once-captured carrier is very small and hence the capture rate can be calculated with the use of the golden rule with the perturbation theory second order in t_{fd} of (2.11). All of the previous theories,¹¹⁻¹⁴ except Ref. 3, are justified only in this nonadiabatic limit,¹⁵⁻¹⁷ as noted also in Sec. I. On the other hand, in the adiabatic

limit the reemission probability is so large that only electrons with very small E_f can be captured by a defect without suffering reemission although t_{fd} , to induce capture, is very large. In this limit we can also interpret the result in such a way that the adiabatic potential of the deep state does not exist within the continuum of the free states because of a strong mixing t_{fd} between the two types of states. This interpretation is in agreement with that based on the Born-Oppenheimer adiabatic approximation in which above the free-electron edge there exists no bound state of $H(Q)$ of (2.4) at any fixed value of Q . This limit cannot be treated with the usual perturbation theory. The capture rate is much different between the two limits.

In the adiabatic limit the capture rate can be obtained without detailed calculation, as shown below. Let us first note that the capture rate R_c is related by the principle of detailed balancing to the emission rate R_e , with which the defect emits an electron to the conduction band.³ This gives

$$R_e = (g_f/g_d)(n_T/n)R_c \exp(-E_d/k_B T), \quad (2.16)$$

with

$$\begin{aligned} n_T &= \frac{1}{g_f V} \sum_f \exp(-E_f/k_B T) \\ &= \left[\frac{m^* k_B T}{2\pi \hbar^2} \right]^{3/2}, \end{aligned} \quad (2.17)$$

where g_f represents the number of equivalent valleys in the conduction band, g_d the number of degeneracy of the deep level, n_T the effective density of states available at a temperature T in a single valley of the conduction band with an effective mass m^* , and n the density of conduction electrons. The capture cross section is defined by

$$R_c = n v_T \sigma, \quad (2.18)$$

with

$$v_T = (3k_B T/m^*)^{1/2}, \quad (2.19)$$

where v_T represents the thermal velocity of an electron. Emission of an electron from the deep state to the free states at high temperatures occurs when the phonon system fluctuates thermally along $V_d(Q)$ from the relaxed configuration at $Q = Q_d$ to the crossing point at $Q = V_d$ between $V_d(Q)$ and $V_f(Q)$ for $E_f = 0$. In the adiabatic limit the emission surely occurs so long as Q exceeds V_d because of a strong t_{fd} . Then we see that the emission rate in the adiabatic limit should be given by a usual formula, familiar in atomic diffusion³¹ and chemical reaction,²⁸ as

$$R_e = (\bar{\omega}/2\pi) \exp[-(E_d + E_A)/k_B T], \quad (2.20)$$

where $\bar{\omega}/2\pi$ represents the attempt frequency and $E_d + E_A$ equals the energy difference between $Q = Q_d$ and $Q = V_d$ along $V_d(Q)$ as seen in Fig. 1. Here $\bar{\omega}$ is given by an average angular frequency of phonons contributing to Q of (2.2). Therefore, in the adiabatic limit the capture cross section should be given by

$$\sigma = \sigma_a \exp(-E_A/k_B T), \quad (2.21)$$

with

$$\sigma_a = (g_d/g_f)(\bar{\omega}/2\pi)/(n_T v_T). \quad (2.22)$$

It will be shown in Sec. IV that this limit is realized when

$$\gamma \gg 1, \quad (2.23)$$

with

$$\gamma \equiv 4\sqrt{B} S k_B T / (3\hbar \bar{\omega} \Delta^{3/2}), \quad (2.24)$$

where B represents the halfwidth of the conduction band. Note that γ approaches ∞ as $\hbar \rightarrow 0$ as it would be.

Chemical reaction,²⁸ atomic diffusion,³¹ and small-polaron hopping in the adiabatic limit¹⁸ have been analyzed by a rate with the same form as (2.20). In this case a convenient guiding principle in the analysis has been given by an expectation that the preexponential factor of the rate should be of the order of 10^{12} – 10^{13} 1/sec. The capture cross section given by (2.21) and (2.22) in the adiabatic limit plays such a role in the present problem since the preexponential factor σ_a of (2.22) does not include any more the interaction strength between the deep and the free states. For $g_d \simeq g_f \simeq 1$ and $\hbar \bar{\omega} \simeq 100$ cm⁻¹, we get that σ_a is about 0.7×10^{-14} (m/m^*) cm² at about 500 K (chosen as a sufficiently high temperature), where m represents the true electron mass. This agrees well with the observation³ of Henry and Lang that the preexponential factor σ_∞ of the capture cross section obtained by high-temperature extrapolation seems to be a universal quantity of the order of 10^{-15} – 10^{-14} cm² for various deep levels within a single host. Therefore we see that the capture process in usual semiconductors with a wide bandwidth is close to the adiabatic limit. In fact this can be justified from the criterion of (2.23) for the adiabatic limit: In usual semiconductors B is of the order of several electron volts, S of several tenth electron volts, and Δ of one electron volt,^{3,32} and hence γ of (2.24) is considerably larger than unity therein.

Reemission of carriers just after capture was first taken into account by Henry and Lang.³ In their treatment, however, the preexponential factor σ_∞ of the capture cross section approaches zero, after

reaching a maximum, as the coupling strength between the deep and the free states is increased.^{5,20} Therefore the adiabatic limit cannot be described by their theory.

In the nonadiabatic limit the preexponential factor σ_∞ of the capture cross section should be much smaller than σ_a of (2.22). We would like to emphasize that the perturbation theory second order in the coupling strength can be used only when $\sigma_\infty \ll \sigma_a$.

III. INTERACTION STRENGTH

The spectral function of interaction between the deep and the free states is defined by

$$\xi(E) = \sum_f |t_{fd}|^2 \delta(E - E_f). \quad (3.1)$$

It is rewritten with the use of (2.11)–(2.14) into a simple form in this section. First it is convenient to rewrite (3.1) into

$$\xi(E) = \langle d | H' \delta(E - H_0(Q)) H' | d \rangle. \quad (3.2)$$

From (2.12) we get for a complex variable z ,

$$\frac{1}{z - H(Q)} = \frac{1}{z - H_0(Q)} + \frac{1}{z - H(Q)} H' \frac{1}{z - H_0(Q)}$$

and

$$\begin{aligned} \frac{1}{z - H(Q)} H' &= \frac{1}{z - H_0(Q)} H' \\ &+ \frac{1}{z - H_0(Q)} H' \frac{1}{z - H(Q)} H'. \end{aligned}$$

Let us take the diagonal element with respect to $|d\rangle$ of these equations. With $E_d(Q) \equiv V_d - Q$ we get from the first one

$$\begin{aligned} \left\langle d \left| \frac{1}{z - H(Q)} H' \right| d \right\rangle \\ = [z - E_d(Q)] \left\langle d \left| \frac{1}{z - H(Q)} \right| d \right\rangle - 1, \end{aligned}$$

from the second one

$$\begin{aligned} \left\langle d \left| H' \frac{1}{z - H(Q)} H' \right| d \right\rangle \\ = [z - E_d(Q)] \left\langle d \left| \frac{1}{z - H(Q)} H' \right| d \right\rangle, \end{aligned}$$

and from an equation which is obtained multiplying the both sides of the second one by H' from the left

$$\begin{aligned}
& \left\langle d \left| H' \frac{1}{z - H_0(Q)} H' \right| d \right\rangle \\
&= \frac{\langle d | H' [z - H(Q)]^{-1} H' | d \rangle}{1 + \langle d | [z - H(Q)]^{-1} H' | d \rangle} \\
&= z - E_d(Q) - \left\langle d \left| \frac{1}{z - H(Q)} \right| d \right\rangle^{-1}. \quad (3.3)
\end{aligned}$$

In describing capture at high enough temperatures it is sufficient to treat the electronic part $H(Q)$ of the total Hamiltonian of (2.3) in a region of $Q \sim V_d$, where $H(Q)$ has no bound state or only a shallow one. This means that we treat a region of Q where $V_d(r)$ is nearly canceled by $g_d(r)Q$ in $H(Q)$ of (2.4). Next, considering that $V_d(r) - g_d(r)Q$ is a localized potential, we neglect all the matrix elements of it except

$$\langle d | V_d(r) - g_d(r)Q | d \rangle \equiv \Delta(Q). \quad (3.4)$$

Then we get from (2.4) with the Koster-Slater method³³

$$\begin{aligned}
& \left\langle d \left| \frac{1}{z - H(Q)} \right| d \right\rangle \\
&= \left[\left\langle d \left| \frac{1}{z - H_F} \right| d \right\rangle^{-1} - \Delta(Q) \right]^{-1}. \quad (3.5)
\end{aligned}$$

Substituting (3.5) into (3.3) we get

$$\begin{aligned}
& \left\langle d \left| H' \frac{1}{z - H_0(Q)} H' \right| d \right\rangle \\
&= z - E_d(Q) + \Delta(Q) - \left\langle d \left| \frac{1}{z - H_F} \right| d \right\rangle^{-1}. \quad (3.6)
\end{aligned}$$

It is very important to note that the imaginary part of this equation does not include Q although the real part includes it.

State $|d\rangle$ is, although localized, not exactly equal to the completely localized Wannier state, and hence $\langle d | \delta(E - H_F) | d \rangle$ does not equal exactly the density-of-state function of the Hamiltonian H_F of the host crystal. But it is a reasonable approximation to assume

$$\begin{aligned}
& \langle d | \delta(E - H_F) | d \rangle \\
&= \begin{cases} \frac{2}{\pi B^2} [E(2B - E)]^{1/2} & \text{for } 0 < E < 2B \\ 0 & \text{otherwise,} \end{cases} \quad (3.7)
\end{aligned}$$

analogously to the hemielliptic approximation³⁴ of

the density-of-state function, where $2B$ represents the total width of the conduction band. Then we get

$$\left\langle d \left| \frac{1}{z - H_F} \right| d \right\rangle = \frac{2}{z - B + [z(z - 2B)]^{1/2}}, \quad (3.8)$$

where the square root is defined to have a positive imaginary part for z with a positive imaginary part. Substituting (3.8) into (3.6), we get $\xi(E)$ of (3.2) as

$$\xi(E) = \begin{cases} [E(2B - E)]^{1/2} / 2\pi & \text{for } 0 < E < 2B \\ 0 & \text{otherwise.} \end{cases} \quad (3.9)$$

Note that (3.9) does not include Q any more although the original definition (3.1) seems to include Q through t_{fd} of (2.11). It also does not include Q_d , and hence it does not depend on at which Q we defined $|d\rangle$, $|f\rangle$, and t_{fd} so long as $|d\rangle$ is localized well.

Since $k_B T \ll 2B$ at usual temperatures, we can use an approximate form of (3.9) as

$$\xi(E) = \begin{cases} \sqrt{BE} / (\sqrt{2}\pi) & \text{for } E > 0 \\ 0 & \text{otherwise.} \end{cases} \quad (3.9')$$

We can estimate an average interaction strength \bar{J} by

$$\begin{aligned}
\bar{J}^2 &\equiv \int \xi(E) \exp(-E/k_B T) dE / (g_f V n_T) \\
&= \pi \sqrt{B} (\hbar^2/m^*)^{3/2} / (g_f V)
\end{aligned}$$

with the use of n_T of (2.17). Since $\hbar^2 \pi^2 (g_f V/N)^{-2/3} / (2m^*)$ is a quantity of the order of $2B$ with N representing the total number of unit cells in the crystal, we see that \bar{J} has a magnitude of the order of B/\sqrt{N} .

IV. FROM NONADIABATIC TO ADIABATIC LIMITS

The capture rate which bridges the nonadiabatic and the adiabatic limits is obtained here. We use a unit of $\hbar=1$ for theoretical convenience in this section except for a case that otherwise is explicitly mentioned. In thermal equilibrium phonons can be described by a density matrix

$$\rho_L = \frac{\exp(-H_L/k_B T)}{\text{Tr}[\exp(-H_L/k_B T)]}, \quad (4.1)$$

determined by the phonon Hamiltonian H_L of (2.1), where Tr means taking a trace over phonon states. We introduce an average amplitude D of thermal fluctuations of the interaction-mode coordinate Q of (2.2) by $D^2 = \text{Tr}(Q^2 \rho_L)$, which gives

$$D^2 = 2S k_B T, \quad (4.2)$$

with the use of S of (2.6) at high temperatures. We introduce further that $\bar{\omega}D$ of thermal fluctuations of

the velocity $v \equiv i[H_L, Q]$ by $\bar{\omega}^2 D^2 = \text{Tr}(v^2 \rho_L)$, which gives also at high temperatures

$$\bar{\omega} = \left[\sum_j V_j^2 \omega_j \right]^{1/2} / \left[\sum_j V_j^2 / \omega_j \right]^{1/2}. \quad (4.3)$$

Note that $\bar{\omega}$ represents an average angular frequency of phonons.

Since $\sum_f a_f^\dagger a_f + a_d^\dagger a_d = 1$, the total Hamiltonian H of (2.3) with its electronic part $H(Q)$ given by (2.12)–(2.14) can be rewritten as

$$H = \sum_f H_f a_f^\dagger a_f + H_d a_d^\dagger a_d + H' \quad (4.4)$$

with

$$H_f = H_L + E_f, \quad H_d = H_L - Q + V_d. \quad (4.5)$$

Note that between phonon Hamiltonians H_f and H_d the value of phonon variables b_j and b_j^\dagger obtained at the lowest-energy lattice configuration is shifted by V_j/ω_j . We first assume that the interaction term H' in (4.4) was switched on at time $t=0$ before which electrons with density n were in thermal equilibrium within the free states. Then the probability with which we find an electron in the deep state at time $t > 0$ is given by

$$N(t) = n g_d / (g_f n_T) \sum_f N_f(t) \exp(-E_f/k_B T), \quad (4.6)$$

with

$$N_f(t) = \text{Tr}(\langle d | e^{-iHt} | f \rangle \rho_L \langle f | e^{iHt} | d \rangle), \quad (4.7)$$

where g_d , g_f , and n_T are the same as used in the detailed-balance relation (2.16). The capture rate R_c can be obtained from

$$N(t) = R_c t \quad \text{for } 2\pi/\bar{\omega} \ll t \quad (\ll R_c^{-1}), \quad (4.8)$$

where $2\pi/\bar{\omega}$ represents an average phonon period.

A quantity with the same structure as $N_f(t)$ of (4.7) was calculated in Ref. 18, although the initial state of transition of an electron was regarded as a single localized one therein while it constitutes a free continuous band in the present problem. In Ref. 18 all the higher-order terms in the perturbational expansion with respect to the interaction to induce a transition were summed up under the condition of $D \gg \bar{\omega}$ where phonons can be treated semiclassically. Note that $N_f(t)$ gives a contribution of an electron occupying initially the f th free state at time $t=0$, and hence it is an infinitesimal quantity of the order of $1/N$. Similarly to Ref. 18, $N_f(t)$ is given by a sum of a series of terms, the first one of which gives the probability of an event in which after

capturing the electron from the f th free state the defect holds the electron without reemission until time t . The second one of the series gives the probability of an event in which, after three successive captures and reemissions, first capturing the electron from the f th free state, then reemitting it into free states, and finally recapturing any one of the free electrons, the defect holds the electron without further reemission until time t , and so on. Note in the second term that three successive captures and reemissions take place in a very short time of the order of a phonon period, since the last reemission and recapture take place, without thermal activation, with the aid of violent lattice vibrations triggered by the first capture of an electron, as explicitly shown in Ref. 18. However, the probability of the last recapture is proportional to the density n of free electrons in the conduction band. Therefore, so long as we confine ourselves to the calculation of the capture rate R_c proportional to the carrier density n at low enough n , it is sufficient to take into account only the first term for $N_f(t)$ mentioned above.

Thus $N_f(t)$ of (4.7) is given by the probability with which the defect captures an electron from the f th free state but does not reemit it into free states during vibrational relaxation just after capture. Then from Ref. 18 we can represent $N_f(t)$ by a sum of diagrams as shown in Fig. 2, where a solid line represents the propagation of an electron at a free state while a dashed one that at the deep state, a dot between them represents the interaction t_{fd} between the two types of states working at times t_1, t_2, \dots and t'_1, t'_2, \dots , and pairs of dots encircled by an ellipse are connected within a time interval of the order of $2\pi/D$ much shorter than the average phonon period $2\pi/\bar{\omega}$. Two solid lines starting at the rightmost circle at time zero are assigned to the f th free state. They are changed in character at every dot and finally end at the leftmost circle at time t with a

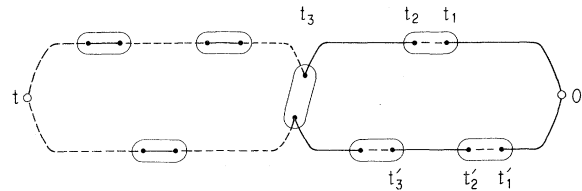


FIG. 2. Diagram contributing to $N_f(t)$. A solid line represents propagation of an electron at a free state, while a dashed one that at the deep state. The two solid lines starting at the rightmost circle at time zero are assigned to the f th free state. Interaction between the free and the deep states works at every dot at times t_1, t_2, \dots and t'_1, t'_2, \dots . Two dots circled by an ellipse move, keeping a short-time interval.

character of the deep state. A horizontal pair represents a virtual interaction (second order in t_{fd} 's) mediated by a state between the two dots of the pair, while the vertical pair represents a real transition of an electron, from a free state to the deep one in Fig. 2. All diagrams to be summed up for $N_f(t)$ have only one vertical pair. However, horizontal pairs located on the right-hand side of the vertical pair represent a higher-order interaction between the free states mediated by the deep state, and they are neglected consistently with the approximation that we neglected phonon effects on the free states in Sec. II. On the other hand, those located on the left-hand side of the vertical pair represent the virtual mixing of the deep state with the free states, and it will be shown below that they contribute to the decrease of the deep-state occupation by reemission just after capture.

The diagram shown in Fig. 2 is defined by the Wigner representation³⁵ of phonon operators, which assigns a real number Q_j to the coordinate operator $b_j + b_j^\dagger$ of the j th phonon, and that P_j to the momentum operator $(b_j - b_j^\dagger)/i$. A time evolution of the coordinate operator (2.2) of the interaction mode is defined by $\exp(iH_L\tau)Q\exp(-iH_L\tau)$, and it has a Wigner representation

$$Q(\tau) = \sum_j V_j (Q_j \cos \omega_j \tau + P_j \sin \omega_j \tau), \quad (4.9)$$

where $Q(0) = \sum_j V_j Q_j$ corresponds to the Wigner representation of the interaction-mode coordinate (2.2) itself. Another time evolution of it defined by $\exp(iH_L\tau) \exp[iH_d(\mu - \tau)]Q \exp[-iH_d(\mu - \tau)] \times \exp(-iH_L\tau)$ with H_d defined by (4.5) has a Wigner representation

$$Q(\mu, \tau) = Q(\mu) + 2 \sum_j \frac{V_j^2}{\omega_j} [1 - \cos \omega_j (\mu - \tau)], \quad (4.10)$$

which evolves obeying the Hamiltonian H_d from τ to μ after it evolved obeying the Hamiltonian H_L from zero to τ . When the diagrams have no horizontal pairs on the right-hand side of the vertical pair, Ref. 18 shows that

$$|t_{fd}|^2 \exp\{-i[Q(\tau) + E_f - V_d]\bar{\tau}\} \quad (4.11)$$

is assigned to the vertical pair with $\tau = \frac{1}{2}(t_1 + t'_1)$ and $\bar{\tau} = t_1 - t'_1$, where t_1 and t'_1 are now times of the two dots of the vertical pair. Assigned to a horizontal pair located on the left-hand side of the vertical pair is

$$- \sum_f |t_{fd}|^2 \exp\{\mp i[Q(\mu, \tau) + E_f - V_d]\bar{\mu}\}, \quad (4.12)$$

where for a pair of dots at times t_{2n} and t_{2n+1} ($> t_{2n}$) for $n=1, 2, \dots$ locating on the upper dashed line we take the upper sign ($-$) in the exponent with $\mu = \mu_n \equiv \frac{1}{2}(t_{2n+1} + t_{2n})$ and $\bar{\mu} = \bar{\mu}_n \equiv t_{2n+1} - t_{2n}$, while for a pair of dots at times t'_{2n} and t'_{2n+1} ($> t'_{2n}$) for $n=1, 2, \dots$ locating on the lower dashed line we take the lower sign ($+$) with $\mu = \mu'_n \equiv \frac{1}{2}(t'_{2n+1} + t'_{2n})$ and $\bar{\mu} = \bar{\mu}'_n \equiv t'_{2n+1} - t'_{2n}$. A product of all these quantities obtained in a diagram is integrated in $\bar{\tau}$ from $-\infty$ to ∞ , in $\bar{\mu}$ from 0 to ∞ , and in τ and μ from 0 to t under the condition of $\tau < \mu_1 < \mu_2 < \dots$ and $\tau < \mu'_1 < \mu'_2 < \dots$, and we sum up contributions of all possible diagrams with various numbers of horizontal pairs. The result is written as

$$A(\{Q_j, P_j\}) = 2\pi \int_0^t d\tau |t_{fd}|^2 \delta(Q(\tau) + E_f - V_d) G(t, \tau), \quad (4.13)$$

with

$$G(t, \tau) = \exp \left[-2\pi \sum_f \int_\tau^t d\mu |t_{fd}|^2 \delta(Q(\mu, \tau) + E_f - V_d) \right]. \quad (4.14)$$

Note that (4.13) is determined by fixing a set of $\{Q_j, P_j\}$ through (4.9) for $Q(\tau)$ and (4.10) for $Q(\mu, \tau)$. The distribution of $\{Q_j, P_j\}$ is given by the Wigner distribution function

$$\rho_w(\{Q_j, P_j\}) = \left[\prod_j \frac{\omega_j}{4\pi k_B T} \right] \exp \left[- \sum_j \frac{\omega_j (P_j^2 + Q_j^2)}{4k_B T} \right], \quad (4.15)$$

which corresponds to the Wigner representation of the density matrix ρ_L of (4.1) obtained at high temperatures for $k_B T \gg \bar{\omega}$. Introducing an average defined by

$$\langle\langle \rangle\rangle = \left[\prod_j \int_{-\infty}^{\infty} dQ_j \int_{-\infty}^{\infty} dP_j \right] \rho_w \{Q_j, P_j\} \dots, \quad (4.16)$$

we get $N_f(t) = \langle\langle A(\{Q_j, P_j\}) \rangle\rangle$. Then from (4.6) we get

$$N(t) = \frac{ng_d}{g_f n_T} 2\pi \int_0^t d\tau \left\langle \left\langle \xi(V_d - Q(\tau)) G(t, \tau) \exp \left[-\frac{V_d - Q(\tau)}{k_B T} \right] \right\rangle \right\rangle, \quad (4.17)$$

where $\xi(E)$ of (3.1) was used to rewrite the sum of $N_f(t)$.

In the nonadiabatic limit the perturbation theory second order in t_{fd} is applicable, which is equivalent to an approximation that $G(t, \tau)$ defined by (4.14) is regarded as unity in (4.17). Now we use that $\langle\langle f(Q(\tau)) \rangle\rangle$ for any function $f(x)$ does not depend on time τ from ergodicity, although it can also be ascertained by explicit calculation with (4.9) and (4.16). Then using (3.9') for $\xi(E)$ and calculating the average in (4.17) with (4.15) and (4.16) we get from (4.8) the capture rate R_c in the nonadiabatic limit by

$$R_c = \frac{ng_d}{g_f n_T} \frac{\sqrt{B} S k_B T}{\hbar \Delta^{3/2}} \exp(-E_A/k_B T), \quad (4.18)$$

in a usual case of $\Delta \gg (2Sk_B T)^{1/2}$, where Δ and E_A are connected with V_d by (2.10) and (2.15), and \hbar was recovered for later convenience. The capture cross section σ of (2.18) is given in this nonadiabatic limit by

$$\sigma = \sigma_{na} \exp(-E_A/k_B T), \quad (4.19)$$

with

$$\sigma_{na} = (g_d/g_f)(\bar{\omega}/2\pi)(3\pi\gamma/2)/(n_T v_T), \quad (4.20)$$

where γ is defined by (2.24). This limit is justified when

$$\gamma \ll 1, \quad (4.21)$$

as will be shown later. Therefore σ_{na} should be much smaller than σ_a of (2.22) which is the saturation value obtained in the adiabatic limit for $\gamma \gg 1$.

In order to proceed beyond the nonadiabatic limit we must take into account that $G(t, \tau)$ is smaller than unity in (4.17). Let us first consider a time when $Q(\tau) + E_f - V_d$ vanishes in the δ function in (4.13). At that time a transition of an electron from the f th free state to the deep state can take place. It is convenient here to interpret $Q(\tau)$ as describing a time evolution of the interaction-mode coordinate on the adiabatic potential $V_f(Q)$ of (2.7) associated with the f th free state, and $Q(\tau) + E_f - V_d$ as representing the difference $V_f(Q(\tau)) - V_d(Q(\tau))$ at $Q = Q(\tau)$. Then two types are possible in the transition, which are illustrated, respectively, in the upper and lower halves of Fig. 3 both for cases (I) and (II) shown, respectively, in the left and right halves. Figure 3 enlarges the crossing region between adiabatic potentials for various free states and that of $V_d(Q)$ for the deep state. In the course of a time evolution of $Q(\tau)$ on $V_f(Q)$ for the f th free state

$V_f(Q(\tau))$ crosses with $V_d(Q(\tau))$ first at time $t_1(E_f)$ upward and again at $t_2(E_f)$ downward after reaching a turning point. In the upper half of Fig. 3 a transition takes place at $t_1(E_f)$ while in the lower half at $t_2(E_f)$. After the transition at $\tau = t_1(E_f)$ or $t_2(E_f)$ the interaction-mode coordinate evolves with time μ ($> \tau$) obeying $Q(\mu, \tau)$ of (4.10) with $Q(\tau, \tau) = Q(\tau)$, where $Q(\mu, \tau)$ describes a time evolution of the interaction-mode coordinate on $V_d(Q)$. It is $Q(\mu, \tau)$ that determines $G(t, \tau)$ of (4.14). In fact τ in (4.14) is fixed at a time satisfying $Q(\tau) + E_f - V_d = 0$ by the δ function in (4.13). Noting $dQ(\mu, \tau)/d\mu = dQ(\tau)/d\tau$ at $\mu = \tau$ we get a trace of the interaction-mode coordinate shown in Fig. 3, which switches from $Q(\tau)$ to $Q(\mu, t_1(E_f))$ or $Q(\mu, t_2(E_f))$ at the crossing times $t_1(E_f)$ or $t_2(E_f)$, respectively. As shown in Fig. 3 we denote by $t'_1(E_f)$ or $t'_2(E_f)$ a time μ at which $Q(\mu, t_1(E_f))$ or $Q(\mu, t_2(E_f))$, respectively, crosses V_d , after which $V_d(Q(\mu, \tau))$ becomes lower than $V_f(Q(\mu, \tau))$ for $E_f = 0$.

In the nonadiabatic limit both types of transitions shown in the upper and the lower halves of Fig. 3 contribute equally to the capture rate since the in-

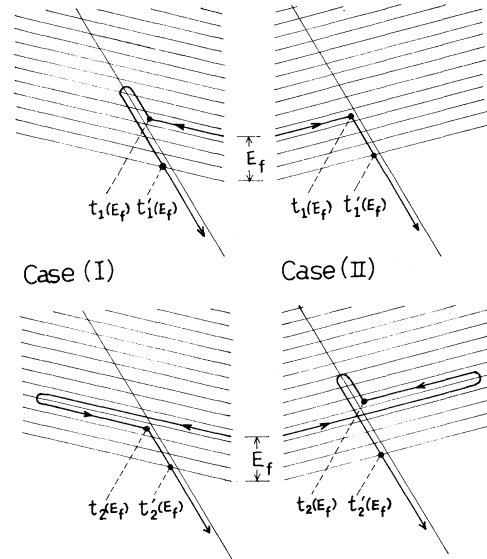


FIG. 3. Two types in capture of a free electron into the deep state, shown, respectively, in the upper and the lower halves for cases (I) and (II) which are shown, respectively, on the left- and the right-hand sides. At time $t_1(E_f)$ or $t_2(E_f)$ an electron makes a transition from the f th free state with energy E_f to the deep state, while at time $t'_1(E_f)$ or $t'_2(E_f)$ the electron gets out of the continuum of the free states and is finally captured.

interaction between the deep and the free states is so small that reemission of once-captured carriers can be neglected. Apart from the nonadiabatic limit, however, contributions of the cases shown in the upper half for case (I) and in the lower half for case (II) decrease steeply: In these cases $Q(\mu, \tau)$ reaches a turning point, where its velocity vanishes, between a time interval of μ from $t_1(E_f)$ to $t'_1(E_f)$ or from $t_2(E_f)$ to $t'_2(E_f)$, and hence we can conclude from the Landau-Zener formula^{23,24} that reemission of once-captured carriers takes place violently around

$$G(t, \tau) = \begin{cases} \exp \left[-2\pi \sum_{\substack{f' \\ (E_{f'} < E_f)}} |t_{f'd}|^2 / (dQ(\tau)/d\tau) \right] & \text{for } dQ(\tau)/d\tau > 0 \\ 0 & \text{otherwise,} \end{cases} \quad (4.22)$$

for t sufficiently larger than $t'_1(E_f)$ and $t'_2(E_f)$. Note that (4.22) is just a product of individual Landau-Zener probabilities with which an electron trapped in the deep state does not make a transition to a free state with energy smaller than E_f . It is convenient here to introduce a function defined by

$$P(E, v) = \begin{cases} \exp[-2\pi\xi(E)/\hbar v] & \text{for } v > 0 \\ 0 & \text{otherwise,} \end{cases} \quad (4.23)$$

with

$$\xi(E) = \int_0^E \xi(E') dE', \quad (4.24)$$

where $\xi(E)$ is defined by (3.1). We will explicitly write \hbar hereafter as in (4.23). Then considering the δ function in (4.13) we can rewrite $G(t, \tau)$ of (4.22) into $P(V_d - Q(\tau), dQ(\tau)/d\tau)$, which is independent of t , so long as t is much larger than an average phonon period.

Now we calculate $N(t)$ of (4.17). Since $Q(\tau)$ of (4.9) and $dQ(\tau)/d\tau$ are perpendicular to each other in the multidimensional space spanned by $\{Q_j, P_j\}$'s, averaging $\langle\langle \rangle\rangle$ in (4.17) can be performed independently for $Q(\tau)$ and $dQ(\tau)/d\tau$. Moreover, both $\langle\langle \delta(E - V_d + Q(\tau)) \rangle\rangle$ and $\langle\langle \delta(v - dQ(\tau)/d\tau) \rangle\rangle$ do not depend on τ because of ergodicity, and they are respectively given from (4.16) by

$$g(E) = \frac{1}{(4\pi S k_B T)^{1/2}} \exp \left[-\frac{(E - V_d)^2}{4S k_B T} \right] \quad (4.25)$$

and

$$f(v) = \frac{1}{\bar{\omega}(4\pi S k_B T)^{1/2}} \exp \left[-\frac{v^2}{4\bar{\omega}^2 S k_B T} \right]. \quad (4.26)$$

The widths of these distribution functions equal,

this turning point. Therefore we take into account hereafter only the cases shown in the lower half for case (I) and in the upper half for case (II) in Fig. 3. They are characterized by the fact that the velocity $dQ(\mu, \tau)/d\mu = dQ(\tau)/d\tau$ at the crossing time $\mu = \tau = t_1(E_f)$ or $t_2(E_f)$ is positive both for cases (I) and (II). Furthermore we approximate the velocity $dQ(\mu, \tau)/d\mu$ during the time interval of μ from $t_1(E_f)$ to $t'_1(E_f)$ or $t_2(E_f)$ to $t'_2(E_f)$ by its initial velocity $dQ(\tau)/d\tau$. Then $G(t, \tau)$ of (4.14) can be rewritten as

respectively, D^2 of (4.2) and $(\bar{\omega}D)^2$ determined by (4.3), as it would be. Thus we get from (4.17) and (4.8) the capture rate R_c as

$$R_c = \frac{ng_d}{g_f n_T} \frac{2\pi}{\hbar} \int_0^\infty dE g(E) e^{-\beta E} \xi(E) \langle P(E, v) \rangle_v, \quad (4.27)$$

with

$$\langle P(E, v) \rangle_v = \int dv f(v) P(E, v), \quad (4.28)$$

and $\beta = 1/k_B T$. Using (2.10) and (2.15) we can rewrite the exponential factor in $g(E)e^{-\beta E}$ into $\exp[-\beta(E_A + \frac{1}{2}E\Delta/S + \frac{1}{4}E^2/S)]$, in which $\frac{1}{4}\beta E^2/S$ in the exponent can be neglected in a usual case of $\Delta^2 \gg S k_B T$. Then R_c of (4.27) can be approximated by

$$R_c = \frac{ng_d}{g_f n_T} \eta \frac{\bar{\omega}}{2\pi} \exp(-E_A/k_B T), \quad (4.29)$$

with

$$\eta = \frac{1}{\hbar \bar{\omega}} \frac{2\pi^{3/2}}{(S k_B T)^{1/2}} \int_0^\infty dE \xi(E) \langle P(E, v) \rangle_v \times \exp \left[-\frac{E\Delta}{2S k_B T} \right]. \quad (4.30)$$

The meaning of η becomes transparent when R_c is transformed to the emission rate R_e by the detailed-balance relation (2.16) as

$$R_e = \eta \frac{\bar{\omega}}{2\pi} \exp[-(E_d + E_A)/k_B T]. \quad (4.31)$$

These equations are common for cases (I) and (II).

In the adiabatic limit the interaction $\xi(E)$ between

the deep and the free states is so strong that we can approximate $\exp(-\frac{1}{2}\beta E\Delta/S)$ in (4.30) by unity compared with $\exp[-2\pi\xi(E)/\hbar v]$ in $P(E, v)$ defined by (4.23). In this limit it is convenient to change the integration variable in (4.30) from E to $\xi(E)$ with the use of $\xi(E)dE = d[\xi(E)]$ obtained from (4.24). Then we get $\eta = 1$, or the emission rate R_e given by (2.20), in the adiabatic limit. Thus the result inferred from a qualitative discussion in Sec. II was ascertained here by an explicit calculation. The at-

tempted frequency $\bar{\omega}/2\pi$ in (2.20) was now determined to be given by (4.3). It is very important to note that the procedure described above to get (2.20) does not depend on an explicit form of the interaction function $\xi(E)$ defined by (3.1).

Next let us use (3.9') for $\xi(E)$ obtained in Sec. III, in order to get η in a general case. Then we can show that η of (4.30) is a function of only one parameter γ defined by (2.24). In fact the E integration in (4.30) gives

$$\eta = \tanh 3\theta \left\{ \tanh 3\theta - \frac{\sinh^2 2\theta}{3 \tanh \theta \cosh^2 3\theta} \ln \left[\frac{\sinh 3\theta}{4 \sinh^3 \theta} \right] - \frac{\cosh 4\theta - 2 \cosh 2\theta}{\sqrt{3} \cosh^2 3\theta} \left[\frac{\pi}{2} + \tan^{-1} \left[\frac{\tanh \theta}{\sqrt{3}} \right] \right] \right\}, \quad (4.32)$$

with θ determined by

$$\sinh 3\theta = (3\sqrt{3}/2)\gamma. \quad (4.33)$$

In the limiting case η tends to

$$\eta \simeq (3\pi/4)\gamma \quad \text{for } \gamma \ll 1, \quad (4.34)$$

and

$$\eta \simeq 1 - (5\pi/9\sqrt{3})\gamma^{-2/3} \quad \text{for } \gamma \gg 1. \quad (4.35)$$

The γ dependence of η is shown in Fig. 4. The capture rate obtained from (4.34) and (4.29) in the non-adiabatic limit for $\gamma \ll 1$ is just the half of that given by (4.18), because we neglected in the calculation of η such trajectories of the interaction-mode coordinate as shown in the upper half of Fig. 3 for case (I) and in the lower half for case (II). But contributions of the neglected trajectories become negligible soon when γ is increased as $\gamma \gtrsim \frac{1}{2}$, as discussed before. Therefore we can use (4.29) and (4.31) with η of (4.32) for a wide range of γ .

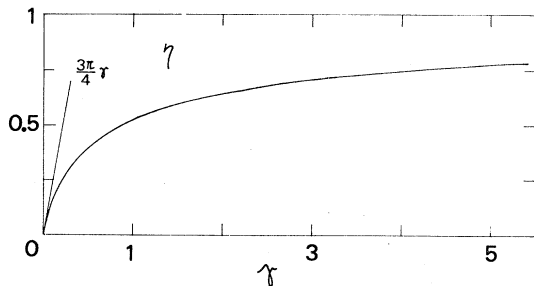


FIG. 4. Parameter η shown as a function of the adiabaticity parameter γ , with which the preexponential factor of the carrier-emission rate is given by η times the attempt frequency $\bar{\omega}/2\pi$.

V. DISCUSSION

When the capture cross section is expressed in a form (1.1) at high temperatures for $k_B T \gg \hbar\bar{\omega}$, the preexponential factor of the capture rate R_c is given by $R_{c\infty} = n v_T \sigma_\infty$ from (2.18) and that of the emission rate R_e by $R_{e\infty} = (g_f/g_d) n_T v_T \sigma_\infty$ from (2.16). Note here $v_T \propto T^{1/2}$ and $n_T V_T \propto T^2$. In many experimental papers it has often been assumed that σ_∞ was independent of temperature. Accordingly the Arrhenius plot of $R_c/T^{1/2}$ or R_e/T^2 has often been used under the assumption of $R_{c\infty} \propto T^{1/2}$ or $R_{e\infty} \propto T^{1/2}$, respectively, in order to get a correction to the activation energy obtained by a simple R_c or R_e vs $1/T$ plot. From the present work, however, this assumption of constancy of σ_∞ cannot be justified. From (2.18) and (4.29) we get

$$\sigma_\infty = \frac{g_d}{g_f n_T v_T} \eta \frac{\bar{\omega}}{2\pi}. \quad (5.1)$$

It was mentioned in Sec. II that the capture process in usual semiconductors can adequately be described by situations close to the adiabatic limit. Then we can regard η in (5.1) as close to unity, almost independent of temperature. This gives $\sigma_\infty \propto T^{-2}$ and $R_{c\infty} \propto T^{-3/2}$, and it is $R_{e\infty}$ being about the attempt frequency $\bar{\omega}/2\pi$ that can be regarded as almost independent of temperature.

At temperatures where $k_B T$ is comparable to $\hbar\bar{\omega}$, distribution functions $g(E)$ and $f(v)$ in (4.25) and (4.26) must be adjusted so as to have a width determined by an effective temperature¹⁸

$$T' \equiv (\hbar\bar{\omega}/2k_B) \coth(\frac{1}{2}\hbar\bar{\omega}/k_B T), \quad (5.2)$$

instead of the real temperature T . In this case we can calculate the capture rate R_c from (4.27) using the corrected distribution functions $g(E)$ and $f(v)$. The emission rate R_e can be obtained from R_c using

the detailed-balance relation (2.16). In this case, however, even if R_c was expressed in a form of (4.29) with $\exp(-E_A/k_B T)$ replaced by $\exp(-E_A/k_B T')$, we cannot express η as a function of only one parameter since $\exp(-\beta E)$ in (4.27) cannot be replaced by $\exp(-E/k_B T')$.

The present formula (4.27) for the capture rate is composed of two important factors $\xi(E)$ and $\langle P(E, \nu) \rangle_\nu$. The former describes the process of initial capture of a free electron to the deep state, while the latter describes the rate with which the electron is not reemitted to free states just after capture. It is sufficient to treat the initial capture process with the perturbation theory second order in the interaction t_{fd} of (2.11), since t_{fd} is an infinitesimal quantity proportional to $N^{-1/2}$. Within the second-order perturbation the static-coupling scheme as adopted here is the most convenient.¹⁵⁻¹⁷ On the contrary, we can say that it is not easy to get an answer correct within second order in t_{fd} in the usual Born-Oppenheimer adiabatic-coupling scheme since the nonadiabaticity operator appearing therein has no direct connection with t_{fd} .³⁶ In this scheme electronic wave functions diagonalizing $H(Q)$ in (2.3) must first be obtained, and t_{fd} 's are completely incorporated in them since $H(Q)$ is given by (2.12). Several theories^{3,11,13,14} presented so far calculate the capture rate in the Born-Oppenheimer adiabatic-coupling scheme treating the nonadiabaticity operator with the non-Condon approximation. If the procedure is performed properly, of course, we can reach a correct answer.¹⁵⁻¹⁷ In some^{3,14} of these, however, electronic wave functions diagonalizing $H(Q)$ are not obtained properly enough, and hence obtained capture rates seem unjustifiable even within second order in t_{fd} .

Within second order in t_{fd} it is not important that

initial states in the capture process constitute a free-electron continuum, since it is sufficient only to average finally an elemental rate of transition from an individual free state to the deep state over various free states. It is for this reason that all the theories presented so far employ the nonradiative transition rate between two localized electronic states, nevertheless, to calculate the rate of capture of free electrons into the localized deep state. When we consider the capture process beyond the second-order perturbation in t_{fd} , however, it becomes much different from the nonradiative transition process between two localized states. The present work is the first to give the capture rate which is applicable beyond the second-order perturbation in t_{fd} and valid in the adiabatic (strong-coupling) limit.

When a defect has a charge before capturing a free carrier, it provides many shallow bound electronic states above a lowest deep state. At high temperatures transitions of electrons between these shallow bound states and the free states are so rapid that the thermal-equilibrium distribution of electrons between them can be regarded as always maintained. This case can also be treated by the present formulation with a small correction. In practice, however, it seems reasonable to describe the capture process in the adiabatic limit since the interaction t_{fd} between a shallow state and the deep state is larger than that between a free state and the deep state and even the capture process without shallow bound states can be considered to be close to the adiabatic limit. In the adiabatic limit the capture process can be described without knowing the interaction t_{fd} : The emission rate R_e is given by (2.20) and the capture rate R_c by (2.16) determined by R_e , where it is necessary only to redefine n_T appearing in (2.16) in such a way that it includes also the shallow bound states in (2.17).

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