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Adiabatic and Non-Adiabatic Limits for Multi-Phonon Capture of Free Electrons by Deep Centers

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The interaction strength between free and deep states is proportional to the free-electron bandwidth 2B at lattice configurations where free states cross with the deep state. A unified expression of the multi-phonon capture rate is given for a center with only one bound state. The pre-exponential factor of the emission rate related with the capture rate by detailed balancing approaches an average phonon frequency f_a in the adiabatic (large B) limit while it is much smaller than f_a in the non-adiabatic (small B) limit.

I. Introduction

Recently free-electron capture by deep centers in semiconductors has attracted much attention both from laser devices and from solid state physics[1]. It gives a typical example of relaxation from free continuous states to a deep bound state with a large lattice distortion around it. However no reliable theory has been presented so far on the multi-phonon capture rate. The present work is devoted to give such a theory for a center with only one bound state under the condition that the electron-phonon interaction can be treated semiclassically at high temperatures.

We know two limits for a transition between two localized electronic states which occurs around a lattice configuration where the adiabatic potential energies associated with these states cross with each other in the course of thermal lattice vibrations[2]. In the non-adiabatic limit the transfer integral between the two states is so small that they are not mixed well quantum-mechanically within the duration time of a crossing event. In the adiabatic limit the opposite is realized. The transition rate is much different between these two limits. In the present problem too, the situation is similar as shown in Fig.(1) which shows the adiabatic potential energies associated with the deep state (a sigle line) and with the free states (multiple lines) along the interaction-mode (or reaction) co-ordinate Q [3]. Here the deep state is lower by energy E_d than the lowest edge, with energy zero, of the free states, while it crosses with the free states above the activation energy E_A for carrier capture. V_d, Δ, and S represent respectively the energy of the deep state at the unrelaxed lattice configuration, the energy difference between the deep and the free states at the relaxed configuration Q_d, and the lattice distortion energy at Q_d. Case (I) on the left half is met usually, but Case (II) on the right half seems realized by a center giving rise to the persistent photoconductivity[4]. Polaron and exciton self-trapping[3] can be classified into Case (II). It will be shown later that the interaction between the deep and the free states at the crossing configurations is stronger for a wider bandwidth of the free states. Most theories[5∿7] on the capture rate presented so far adopt the second-order perturbation in the interaction strength, which is applicable only in the non-adiabatic (small bandwidth) limit. However it is an open problem whether the perturbational approach is applicable or not to most semiconductors whose bandwidth is very wide of the order of several electron volts. If not, we must take into account re-emission of once captured carriers into free states. The effect was first taken into account by Henry and Lang[8], but their treatment is too approximated to be acceptable. Moreover they calculated the rate of initial capture before

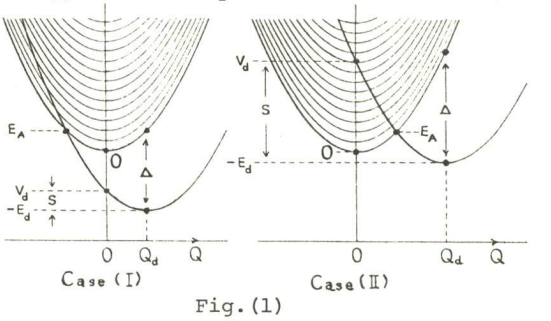

Fig.(1)

re-emission as if the free-electron continuous states were a sigle level by using the theories[2,9,10] on a transition between two localized electronic states. The situation is the same also in ref.(7). Besides these, the matrix element to induce capture is quite different depending on different authors.

The emission rate W_e from the relaxed deep state is related with the capture rate W_c by detailed balancing[6,8], as

$$W_c = \frac{n_d}{n_T} W_e \exp(\beta E_d), \quad \text{with} \quad n_T \equiv \frac{1}{V}\sum_k \exp(-\beta E_k) = \left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2}, \tag{1.1}$$

and $\beta = 1/k_B T$, where n_d, V, and $E_k \equiv \hbar^2|k|^2/2m^*$ represent respectively the deep-center concentration, the crystal volume, and the energy of a free electron with effective mass m^* and momentum k. The quantity n_T represents the effective concentration of free-electron states available at T. The emission rate should have a special form in the adiabatic (large bandwidth) limit: Here the deep state is mixed well with the free states at the crossing configurations shown in Fig.(1), and hence an electron activated once to the crossing region from the relaxed deep state is surely emitted to free states. Then we should have in the adiabatic limit

$$W_e = f_a \exp[-\beta(E_d + E_A)], \tag{1.2}$$

where f_a called the attempt frequency is a constant independent of both the temperature and the bandwidth and is given by an average frequency of phonons contributing to the interaction mode. A reliable theory should correctly describe the adiabatic limit mentioned above when the bandwidth is increased enough.

II. Interaction Strength

It is reasonable to assume that electrons interact strongly with phonons only in the deep state localized well. Without a deep center we have free electrons and phonons, described respectively by Hamiltonians H_F and H_L, and no interaction between them. A deep center gives rise to a localized potential which is written as $V_d(r)$ with the electron co-ordinate r in the undistorted lattice and as $V_d(r) - Q g_d(r)$ in a lattice distorted by Q around the deep center. Q defines the interaction mode and can be expressed by a linear combination of various normal-mode co-ordinates, as

$$Q = \sum_k V_k^* (b_k + b_{-k}^\dagger), \quad \text{for} \quad H_L = \sum_k \hbar\omega_k \left(b_k^\dagger b_k + \frac{1}{2}\right), \tag{2.1}$$

with $V_{-k}^* = V_k$, where b_k represents the annihilation operator of a phonon with energy $\hbar\omega_k$ and momentum k. For $k_B T$ larger than the average phonon energy, Q can be regarded as a c-number fluctuating thermally. Then the Hamiltonian for an electron at a fixed Q is given by $H(Q) = H_F + V_d(r) - Q g_d(r)$. When the deep state is occupied, the surrounding lattice is distorted by Q_d as shown in Fig.(1). The deep-state wave function $|d\rangle$ is defined as diagonalizing $H(Q_d)$, as $H(Q_d) = \sum_f E_f a_f^\dagger a_f - \Delta a_d^\dagger a_d$, where a_d and a_f represent respectively the annihilation operator of an electron occupying the deep state and the f-th delocalized state with energy E_f ($\geqq 0$) whose wave function is denoted by $|f\rangle$. We assume that free electrons before capture can be regarded as having wave functions $\{|f\rangle\}$. To be rigorous, we must determine the free-state wave functions by diagonalizing $H(Q=0)$, but this approximation is good for $E_f \lesssim k_B T$ so long as $|V_d|$ and Δ in Fig.(1) are both much larger than $k_B T$. We neglect $\langle f| g_d(r) |f'\rangle$ which is of the order of the inverse of the total number N of unit cells in the crystal, and the interaction mode is chosen such that $\langle d| g_d(r) |d\rangle = 1$. Thus we get

$$H(Q) = H_0(Q) + H'(Q), \quad \text{with} \quad \begin{cases} H_0(Q) = \sum_f E_f a_f^\dagger a_f + (V_d - Q) a_d^\dagger a_d, \\ H'(Q) = \sum_f (t_{fd} a_f^\dagger a_d + t_{fd}^* a_d^\dagger a_f), \end{cases} \tag{2.2}$$

where $V_d = Q_d - \Delta$ and $t_{fd} = (Q_d - Q)\langle f| g_d(r) |d\rangle$ ($\propto 1/\sqrt{N}$). The adiabatic potentials for the f-th free state and the deep state are written as

$$V_f(Q) = E_f + Q^2/(4S) \quad \text{and} \quad V_d(Q) = (Q - 2S)^2/(4S) - E_d, \tag{2.3}$$

with $S = \sum_k |V_k|^2/\hbar\omega_k$, $Q_d = 2S$ and $E_d = S - V_d$. They have been shown in Fig.(1).

$V_f(Q)$ for $E_f = 0$ crosses with $V_d(Q)$ at $Q = V_d$. Then free-electron capture takes place at $Q \sim V_d$ with the activation energy E_A given by $V_d^2/4S$. We introduce here a spectral function for the interaction strength between the deep and the free states

$$\xi(E) = \sum_f |t_{fd}|^2 \delta(E - E_f). \tag{2.4}$$

From (2.2) we can get a relation

$$\langle d|\, H'(Q)\,[\,z - H_0(Q)\,]^{-1} H'(Q)\,|d\rangle = z + Q - V_d - \langle d|\,[\,z - H(Q)\,]^{-1}\,|d\rangle^{-1}, \tag{2.5}$$

for $z = E + i\delta$ with $\delta = +0$. Hamiltonian $H(Q)$ can be devided also into H_F plus the scattering potential $V_d(r) - Q g_d(r)$ of the deep center, and the potential is weak at $Q \sim V_d$ since $H(Q)$ has no bound state there or at most a very shallow one. Then, we can neglect all matrix elements of the potential except $\Delta(Q) \equiv \langle d|V_d(r) - Q g_d(r)|d\rangle$, and we get

$$\langle d|\,[\,z - H(Q)\,]^{-1}\,|d\rangle = [\,G_F(z)^{-1} - \Delta(Q)\,]^{-1}, \tag{2.6}$$

at $Q \sim V_d$, with $G_F(z) = \langle d|\,[\,z - H_F\,]^{-1}\,|d\rangle$. Now we assume that a spectral function $\rho(E) \equiv \langle d|\,\delta(E - H_F)\,|d\rangle$ is written as $2/(\pi B^2)\sqrt{E(2B-E)}$ for $0 < E < 2B$ and zero otherwise by using the half width B of the free-electron band. It satisfies correctly $\int \rho(E)\,dE = 1$. Then we get

$$G_F(z) = \int dE'\,\rho(E')/(z - E') = 2\,[\,z + \sqrt{(z-B)^2 - B^2}\,]^{-1}, \tag{2.7}$$

and the imaginary part of (2.5) gives at $Q \sim V_d$

$$\xi(E) = \frac{1}{2\pi}\sqrt{E(2B-E)}, \quad \text{for } 0 < E < 2B, \text{ and zero otherwise,} \tag{2.8}$$

which is about $\sqrt{2BE}/2\pi$ for $0 < E \lesssim k_B T$ ($\ll 2B$). Function $\xi(E)$ thus determined is independent of Q so long as $Q \sim V_d$. The average value $\bar{J}$ of the interaction strength between the deep and the free states at $Q \sim V_d$ is determined by $\bar{J}^2 = \int \xi(E)\, e^{-\beta E}\,dE / (Vn_T)$, which is about $\pi\hbar^3\sqrt{B/m^{*3}}/V$, with n_T defined by (1.1). Since $\hbar^2\pi^2(N/V)^{2/3}/2m^*$ is of the order of 2B, we see that $\bar{J}$ has a magnitude of the order of $B/\sqrt{N}$.

III. Capture and Emission Rates

Capture of a free electron by the deep center is fulfiled when an electron captured once remains in the deep state without suffering re-emission into free states. For initial capture from an individual free state we can use the theories[2,9,10] on the transition rate between two electronic states in the non-adiabatic limit, since the individual interaction strength is infinitesimal. Then the initial capture rate from the f-th free state is given by

$$W(E_f) = |t_{fd}|^2 R(E_f), \quad \text{with} \quad R(E) = \sqrt{\frac{\pi}{\hbar^2 S k_B T}}\,\exp[\,-\frac{(V_d - E)^2}{4Sk_BT}\,]. \tag{3.1}$$

Here the activation energy $(V_d - E_f)^2/4S$, which is different for different free states as apparent also in Fig.(1), equals the lattice distortion energy at $Q = V_d - E_f$ where $V_f(Q)$ and $V_d(Q)$ in (2.3) cross with each other. After initial capture the interaction-mode co-ordinate Q evolves along a trace shown in Fig.(2) which enlarges the crossing region in Fig.(1). The time evolution of Q is classified into two types shown on the upper and the lower halves for each of Case (I) and Case (II). When i = 1 or 2, initial capture occurs at time $t_i(E_f)$, and subsequently at time $t_i'(E_f)$ the adiabatic potential energy $V_d(Q)$ becomes lower than $V_f(Q)$ for $E_f = 0$ in the course of the time evolution of Q. Time $t_1(E_f)$ is earlier than $t_2(E_f)$. Time interval $\Delta t_i(E_f) \equiv t_i'(E_f) - t_i(E_f)$ during which the deep state is embeded in the free state continuum is longer for i = 1 in Case (I) and for i = 2 in Case (II) than for i = 2 in Case(I) and for i = 1 in Case (II) respectively. Moreover, along these longer-$\Delta t_i(E_f)$ traces, the time derivative of Q (say the velocity), which equals the time derivative of $V_{f'}(Q) - V_d(Q)$ for any f', passes through zero once during $\Delta t_i(E_f)$. Therefore we see from the Landau-Zener formula[11] that re-emission of once-captured electrons occurs violently during $\Delta t_i(E_f)$ for i = 1 in Case (I) and for i = 2 in Case (II), and hence these types of traces of Q are excluded to calculate the capture rate. We assume that the velocity is nearly constant with a magnitude v during $\Delta t_i(E_f)$ for i = 2 in Case (I) and for i = 1 in Case (II). Then the Landau-Zener formula gives the probability that an electron captured once from the f-th free state is not re-emitted to free states, as

$$P(E_f, v) = \frac{1}{2}\exp[\,-2\pi \sum_{(E_{f'}<E_f)} |t_{f'd}|^2/\hbar v\,], \quad \text{or}$$

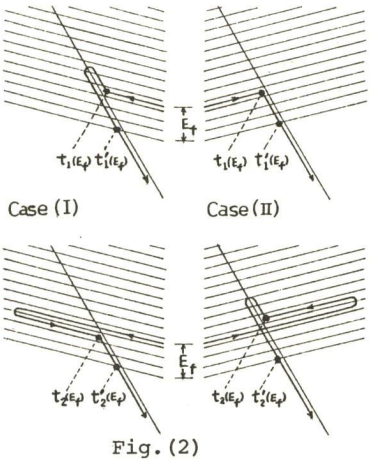

Fig.(2)

$$P(E_f, v) = \frac{1}{2}\exp[-2\pi\zeta(E_f)/\hbar v], \quad \text{with} \quad \zeta(E) = \int_0^E \xi(E')\,dE'. \tag{3.2}$$

The capture rate is the thermal average of $W(E_f)P(E_f, v)$ with respect to E_f and v.

We introduce the velocity operator of the interaction mode by $\hat{v} = i[H_I, Q]/\hbar$, which is written as $\sum_k \omega_k V_k^*(b_k - b_{-k}^\dagger)/i$ by using (2.1). Then the thermal average value of $\hat{v}^2$ is given by $2\bar{\omega}^2 S k_B T$ at high temperatures, where $\bar{\omega}$ defined by

$$\bar{\omega} = \sqrt{\sum_k |V_k|^2 \omega_k} \Big/ \sqrt{\sum_k |V_k|^2 / \omega_k}, \tag{3.3}$$

is an average angular frequency of phonons contributing to the interaction mode. Then the capture rate is given by

$$W_c = \frac{n_d}{n_T}\int dE\, \xi(E)\, e^{-\beta E} R(E) \langle P(E,v)\rangle_v, \quad \text{with} \quad \langle\cdots\rangle_v = \frac{1}{\bar{\omega}\sqrt{\pi S k_B T}}\int_0^\infty dv \cdots \exp[-\frac{v^2}{4\bar{\omega}^2 S k_B T}], \tag{3.4}$$

where $\langle\cdots\rangle_v$ represents the thermal average in v and a finite concentration n_d of deep centers is taken into account. The exponential factor in $e^{-\beta E}R(E)$ can be approximated by $\exp[-\beta E\Delta/2S - \beta E_A]$ for $E \lesssim k_B T \ll \Delta$. Then the emission rate derived from (1.1) and (3.4) is written as

$$W_e = \eta\,\frac{\bar{\omega}}{2\pi}\exp[-\beta(E_d + E_A)], \tag{3.5}$$

with

$$\eta = \frac{\pi^{3/2}}{\hbar\bar{\omega}\sqrt{S k_B T}}\int_0^\infty dE\, \xi(E)\exp[-\frac{E\Delta}{2S k_B T}] \left\langle \exp[-\frac{2\pi\zeta(E)}{\hbar v}]\right\rangle_v \tag{3.6}$$

When $\xi(E)$ is approximated by (2.8), η is given by

$$\eta = \tanh 3\theta\,[\tanh 3\theta - \frac{\sinh^2 2\theta}{3\tanh\theta\cosh^2 3\theta}\ln(\frac{\sinh 3\theta}{4\sinh^3\theta}) - \frac{\cosh 4\theta - 2\cosh 2\theta}{\sqrt{3}\cosh^2 3\theta}\{\frac{\pi}{2} + \mathrm{Tan}^{-1}(\frac{\tanh\theta}{\sqrt{3}})\}], \tag{3.7}$$

with

$$(2\sqrt{3}/9)\sinh 3\theta = 4\sqrt{B S k_B T}/(3\hbar\bar{\omega}\Delta^{3/2}) \equiv \gamma. \tag{3.8}$$

The γ dependence of η is shown in Fig.(3), where in the limiting cases

$$\eta \simeq \frac{3\pi}{4}\gamma, \quad \text{for} \quad \gamma \ll 1, \quad \text{and} \quad \eta \simeq 1 - \frac{5\pi}{9\sqrt{3}}\gamma^{-2/3}, \quad \text{for} \quad \gamma \gg 1. \tag{3.9}$$

In the non-adiabatic limit for $\gamma \ll 1$, we can get $\eta \simeq 3\pi\gamma/4$ also from (3.6) directly by an approximation $\exp[-2\pi\zeta(E)/\hbar v] \simeq 1$, that is, by the second-order perturbation in the interaction Hamiltonian $H'(Q)$. In this limit η should be much smaller than unity, and hence the pre-exponential factor of the emission rate W_e of (3.5) should be much smaller than the average phonon frequency. In the adiabatic limit for $\gamma \gg 1$ we can get $\eta \simeq 1$ also from (3.6) directly by an approximation $\exp[-E\Delta/(2S k_B T)] \simeq 1$ and a relation $d\zeta(E)/dE = \xi(E)$ only. Therefore the result does not depend on the approximation (2.8) for $\xi(E)$. In this limit (3.5) tends to (1.2) and the attempt frequency f_a is given by $\bar{\omega}/2\pi$ with $\bar{\omega}$ determined by (3.3).

The capture cross section σ has traditionally been used by many experimentalists instead of the capture rate. In the adiabatic limit we should have $\sigma = \bar{\omega}/(2\pi n_T v_T) \times \exp(-\beta E_A)$ by using the thermal velocity of free electrons $v_T \equiv \sqrt{3k_B T/m^*}$, where the pre-exponential factor is about 4×10^{-14} cm^2 at about room temperature when m^* is about half the bare electron mass and $\hbar\bar{\omega}$ is about 100 cm^{-1}. The pre-exponential factors of the order of $10^{-15} \sim 10^{-14}$ cm^2 of σ have often been observed at about room temperature[8]. We see from Fig.(3) that these values are located intermediate between those which should be obtained in the non-adiabatic and the adiabatic limits. We can get (3.6) also by summing up all the dominant terms in the perturbational expansion, as will be shown elsewhere.

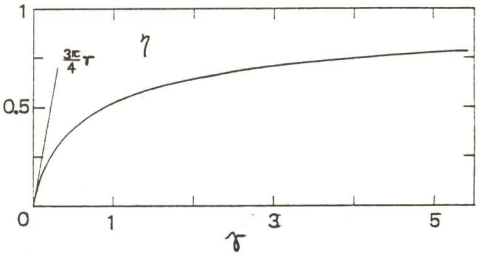

Fig.(3)

1) For example, see D. V. Lang: the same proceedings. 2) T. Holstein: Ann. Phys. 8 (1959) 343; and see also H. Sumi: J. Phys. Soc. Jpn. 49 (1980) no.5. 3) H. Sumi and Y. Toyozawa: J. Phys. Soc. Jpn. 31 (1971) 342. 4) D. V. Lang, R. A. Logan and M. Jaros: Phys. Rev. B 19 (1979) 1015. 5) É. P. Sinyavskii and V. A. Kovarskii: Soviet Phys. - Solid State 9 (1967) 1142. 6) R. Pässler: Phys. Status Solidi (b) 68 (1975) 69 and 85 (1978) 203. 7) B. K. Ridley: J. Phys. C 11 (1978) 2323. 8) C. H. Henry and D. V. Lang: Phys. Rev. B 15 (1977) 989. 9) K. Huang and A. Rhys: Proc. Roy. Soc. A 204 (1950) 406. 10) R. Kubo and Y. Toyozawa: Progr. theor. Phys. 13 (1955) 160. 11) L. D. Landau: Phys. Z. Sowjetunion 1 (1932) 88; and C. Zener: Proc. Roy. Soc. A 137 (1932) 696.