14 time resolved spectroscopy 2 ~rate equation~

Usually, decay curve of luminescence is decayed by exponential. Here, it is explained that why the decay curve is decayed by exponential and how to analyze the decay curve.

14.1 simple model

A number of electrons at excitation condition of E_{ex} is defined as $n(t)$ ($1/cm^3$). It is assumed that electrons at ground state of E_g is excited to E_{ex} per unit time $g(t)$ ($1/cm^3 \cdot$ sec) and the excited electrons are radiative-recombined with transition probability of $\gamma = 1/\tau$ (1/sec). Where, a reciprocal number of the transition probability is assumed as radiative life time of $\tau = 1/\gamma$ (sec),
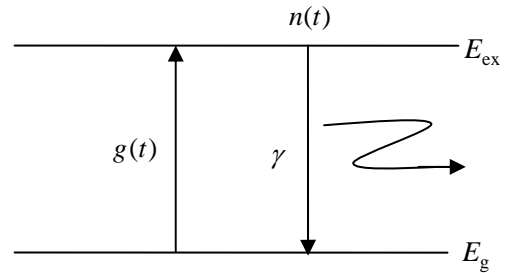

Fig. 14-1 simple model

that is, τ this is a time during luminescence intensity decreasing from an initial intensity to $1/e = 36.8\%$ of the initial intensity.

In this case, varying of the electron density per unit time can be expressed a an rate equation as shown in eq (14.1),

$$\frac{dn(t)}{dt} = g(t) - \gamma\, n(t) \,. \qquad (14.1)$$

The electron density is assumed as n_0, if the electrons are excited at $t = 0$ within a time much shorter than life time. The excitation is finished at a moment, therefore it is assumed that $g(t) = 0$,

$$\int \frac{1}{n(t)} dn(t) = \int -\gamma\, dt \,. \qquad (14.2)$$

From eq (14.2)

$$\ln n(t) = -\gamma\, t + \text{const} = \ln n(t) = -t/\tau + \text{const} \rightarrow n(t) = C\exp(-t/\tau) \,. \qquad (14.3)$$

Where at $t = 0$, $n(0) = n_0$ is satisfied, therefore

$$n(t) = n_0 \exp(-t/\tau) \,. \qquad (14.4)$$

In this simple model, it is assumed that all excited electrons are recombined and the luminescence intensity is simply proportional to a number of the recombined electrons, and then time dependence of the luminescence intensity is expressed by eq. (14.4). Therefore the luminescence exponentially decreases. From eq. (14.4), the graph, which vertical axis is natural log of the luminescence decay curve and horizontal axis is time, becomes straight line and a reciprocal number of a gradient of the graph becomes the life time of the luminescence.

14.2 example of actual observation result

In actually, as show in Fig. 14-1, luminescence process contains not only excitation and radiative recombination processes but also many other processes. Figure 14-2 shows steady state excitation luminescence (excited by continuous wave laser) and pulse excited luminescence (the sample is excited by very intense excitation source momentarily) from $CuGaS_2$. By the pulse excitation, since spectral width is widen, therefore free exciton-polariton luminescence and bound exciton luminescence become one lump. One the other hand, by the steady state excitation, free exciton (FE)- pulariton(upper branch porariton (UBP), lower porariton (LBP)) and bound exciton luminescence I_b, I_c are separated. Figure 14-3 shows time resolved spectrum of free exciton and

bound excitons from $CuGaS_2$. As shown in Fig. 14-3, radiative life time of free exciton is shorter than that of the bound excitons. Figure 14-4(a) and (b) shows temperature dependence of the luminescence decay curve of I_b and I_c bound excitons. It is found that both life time decreases as temperature increasing.
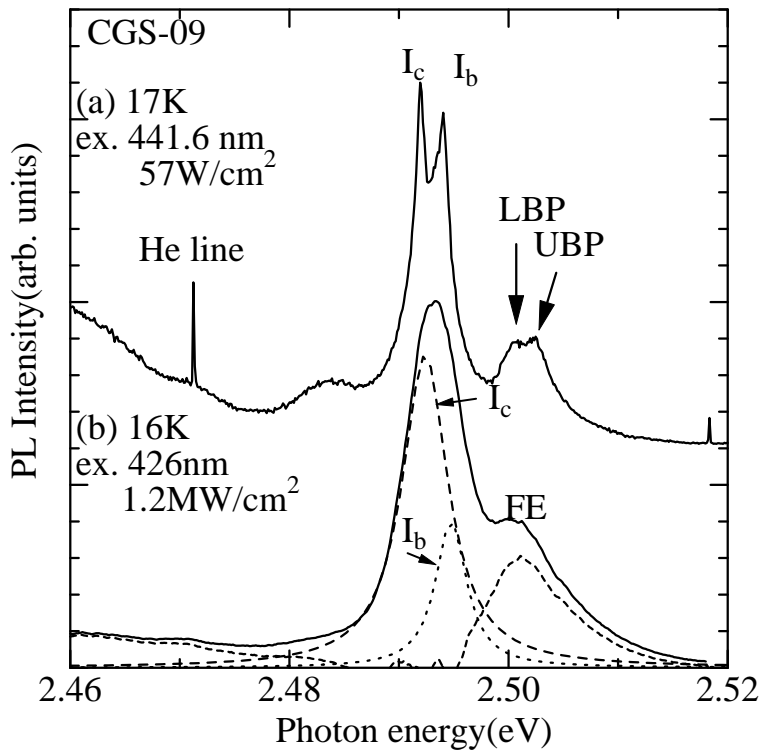

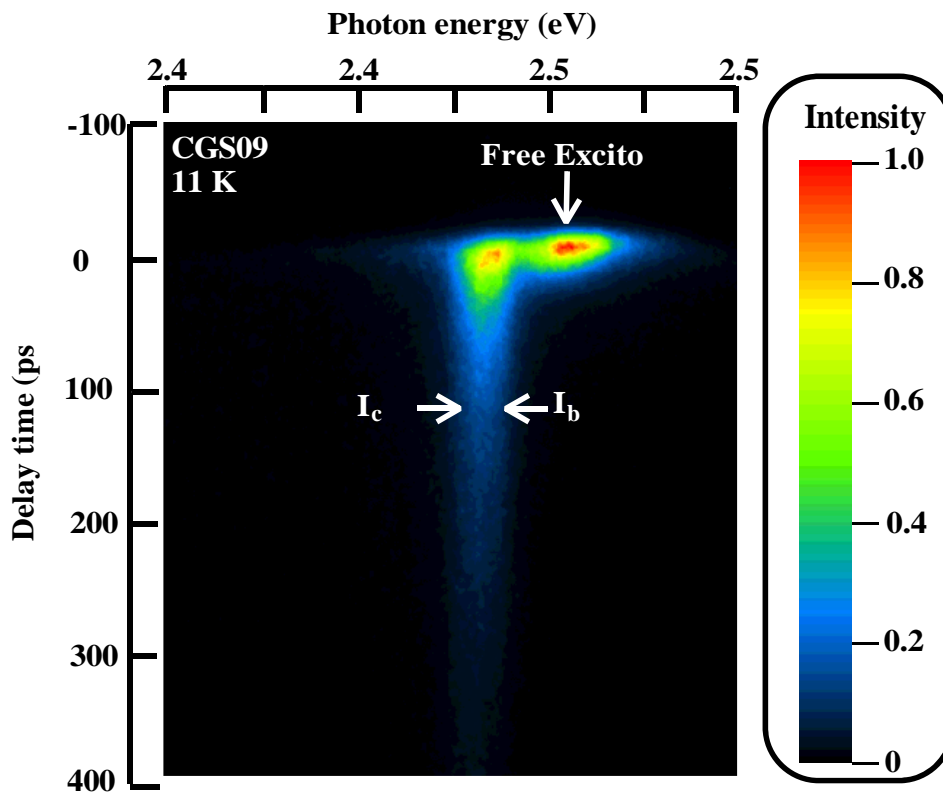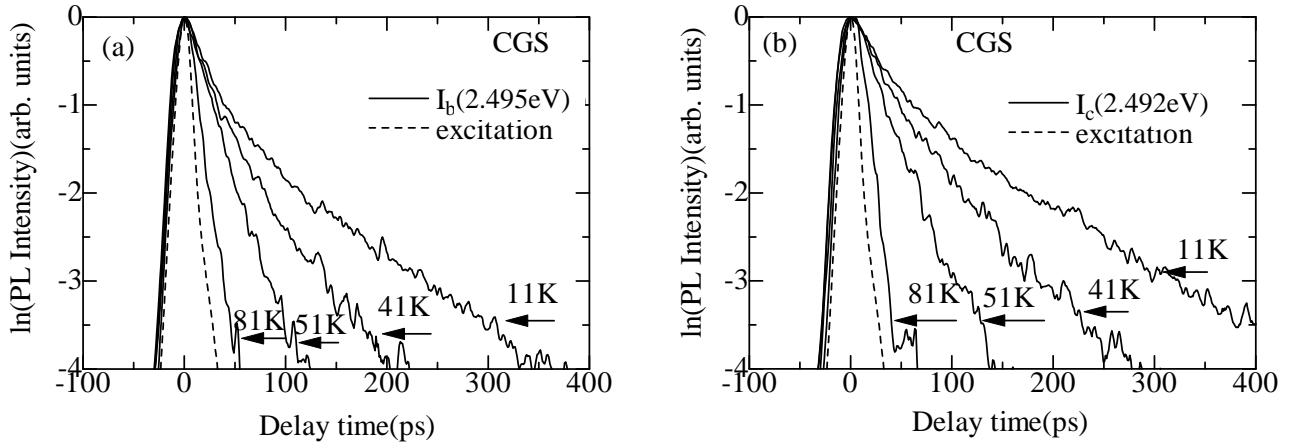Fig. 14-2 steady sate excitation (a) and pulse excitation (b) exciton luminescence

Fig. 14-3 time resolved exciton luminescence

Fig. 14-4 temperature dependence of decay curves of (a)I_b and (b) I_c bound excitions

Let consider the rate equation concretely. Here, parameters are assumed as follows. n_F, n_{Ii} (i=b or c) : density of the free and bound excitons, w_{FIi} : ratio that the free exciton is captured by capture center (such as impurity) and becomes the bound exciton, w_{IiF} : ratio that the bound exciton becomes free exciton again by thermal excitation, $g(t)$: ratio that the free exciton generation by pulse laser excitation, γ_F : ratio of free exaction recombination that is sum of free exciton radiative recombination ratio γ_{Fr} $(= \tau_{Fr}^{-1})$ and non-radiative recombination ratio γ_{Fnr} $(= \tau_{Fnr}^{-1})$ γ_{Ii} : bound excition recombination rate that is sum of bound excition radiative recombination ratio γ_{Iir} $(= \tau_{Iir}^{-1})$ and bound excition non-radiative recombination ratio γ_{Iinr} $(= \tau_{Iinr}^{-1})$, E_{Ii} : binding energy of the bound
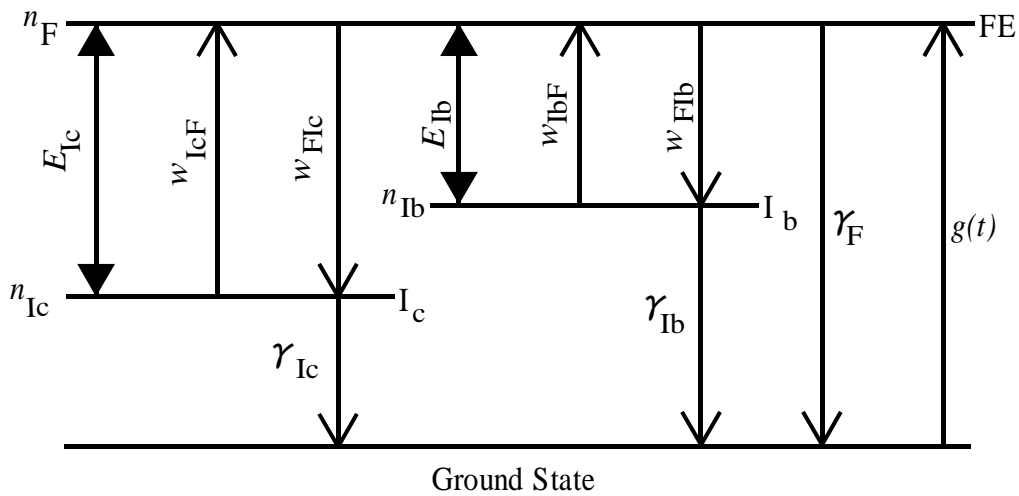

Fig. 14-5 exciton generation and annihilation model

excition I_i, n_G : a number of carriers at the ground state, N_{Ai} : density of free exciton capture center.

From Fig. 14-5 rate equations of excition generation and annihilation are expressed as

$$\frac{dn_F}{dt} = g(t) - \gamma_F n_F - w_{FIc}\left(1 - \frac{n_{Ic}}{N_{Ac}}\right)n_F + w_{IcF}n_{Ic} - w_{FIb}\left(1 - \frac{n_{Ib}}{N_{Ab}}\right)n_F + w_{IbF}n_{Ib}, \tag{14-5}$$

$$\frac{dn_{Ic}}{dt} = -\gamma_{Ic}n_{Ic} + w_{FIc}\left(1 - \frac{n_{Ic}}{N_{Ac}}\right)n_F - w_{IcF}n_{Ic}, \tag{14-6}$$

$$\frac{dn_{Ib}}{dt} = -\gamma_{Ib} n_{Ib} + w_{FIb}\left(1 - \frac{n_{Ib}}{N_{Ab}}\right) n_F - w_{IbF} n_{Ib}, \tag{14-7}$$

$$\frac{dn_G}{dt} = -g(t) + \gamma_{Ic} n_{Ic} + \gamma_{Ib} n_{Ib} + \gamma_F n_F. \tag{14-8}$$

Here, as a representative of equations, eq. (14-5) will be explained.

● $\dfrac{dn_F}{dt}$: a number of free excition increment per unit time

● $g(t)$: it is assumed that all excited electrons are converted into free exciton. Sign of this parameter is pulse because a number of free excition increases.

● $-\gamma_F n_F$: free excitons are annihilated by recombination with transition ratio γ_F. Sign of this term is minus because a number of free excion decreases.

● $-w_{FIc}\left(1 - \dfrac{n_{Ic}}{N_{Ac}}\right) n_F$: free exaction becomes bound excition Ic by captured capture center with ratio w_{FIc}.

Since the capture center can capture only one free exciton, a number of the capture center must be decreased by one as the capture center captures one free exciton. When the capture center captures free exciton and the free exciton becomes a bound exciton, a bound exciton capture ratio to a number of all capture centers N_{Ac} is n_{Ic}/N_{Ac}. If all of the ratio is 1, that is 100%, the remained free exciton capture ratio is n_{Ic}/N_{Ac}. Since free exciton is decreased by capture, sign of this term is minus.

● $w_{IcF} n_{Ic}$: the bound exciton becomes free exciton again by thermal excitation with ratio w_{IcF}. Sign on this term is pulse because a number of the free exciton increases.

You can understand other eqs. (14-6)～(14-8), if you consider theses equations like the above.

14.3 solution of the rate equations

① intensity of the time integrated exciton luminescence spectrum

If excitation intensity is week, a number of free exciton is little, and therefore $n_{Ic} \ll N_{Ac}$, $n_{Ib} \ll N_{Ab}$ are satisfied. In this case, eqs. (14-5)~(14-8) become linear differential equations. Therefore, time integrated PL (variation of PL is summed in time domain) is as same as steady state PL. In the steady state PL process, excitation and recombination are always occurred, that is this process is equilibrium state, therefore $dn/dt = 0$ is satisfied. From the above, in the steady state with weak excitation, it is assumed that $n_{Ib} \ll N_{Ab}$ and $n_{Ic} \ll N_{Ac}$,

$$0 = g(t) - \gamma_F n_F - w_{FIc} n_F + w_{IcF} n_{Ic} - w_{FIb} n_F + w_{IbF} n_{Ib}$$
$$= g(t) - (w_{FIc} + w_{FIb} + \gamma_F) n_F + n_F + w_{IcF} n_{Ic} + w_{IbF} w_{IcF} n_{Ib}, \tag{14-9}$$

$$0 = -\gamma_{Ic} n_{Ic} + w_{FIc} n_F - w_{IcF} n_{Ic}, \tag{14-10}$$

$$0 = -\gamma_{Ib} n_{Ib} + w_{FIb} n_F - w_{IbF} n_{Ib}. \tag{14-11}$$

From eq. (14-8)

$$0 = -g(t) + \gamma_F n_F + \gamma_{Ic} n_{Ic} + \gamma_{Ib} n_{Ib},$$

$$n_F = \frac{g(t) - \gamma_{Ic} n_{Ic} - \gamma_{Ib} n_{Ib}}{\gamma_F}. \tag{14-12}$$

Into eq. (14-10), eq. (14-12) is substituted,

$$0 = -\gamma_{Ic} n_{Ic} - w_{IcF} n_{Ic} + w_{FIc}\left(\frac{g(t) - \gamma_{Ic} n_{Ic} - \gamma_{Ib} n_{Ib}}{\gamma_F}\right). \tag{14-13}$$

$$\left(\gamma_{Ic} + w_{IcF} + \frac{w_{FIc}\gamma_{Ic}}{\gamma_F}\right)n_{Ic} + \frac{w_{FIc}\gamma_{Ib}}{\gamma_F}n_{Ib} = \frac{w_{FIc}g(t)}{\gamma_F}. \tag{14-14}$$

Into eq. (14-11), eq. (14-12) is substituted

$$0 = -\gamma_{Ib} n_{Ib} - w_{IbF} n_{Ib} + w_{FIb}\left(\frac{g(t) - \gamma_{Ic} n_{Ic} - \gamma_{Ib} n_{Ib}}{\gamma_F}\right). \tag{14-15}$$

$$\left(\gamma_{Ib} + w_{IbF} + \frac{w_{FIb}\gamma_{Ib}}{\gamma_F}\right)n_{Ib} + \frac{w_{FIb}\gamma_{Ic}}{\gamma_F}n_{Ic} = \frac{w_{FIb}g(t)}{\gamma_F}. \tag{14-16}$$

From eq. (14-14),

$$n_{Ic} = w_{FIc}\frac{g(t)}{\gamma_F}\frac{1}{\gamma_{Ic} + w_{IcF} + \frac{w_{FIc}\gamma_{Ic}}{\gamma_F}} - \frac{w_{FIc}\gamma_{Ib}}{\gamma_F}\frac{1}{\gamma_{Ic} + w_{IcF} + \frac{w_{FIc}\gamma_{Ic}}{\gamma_F}}n_{Ib}$$

$$= \frac{1}{\gamma_{Ic} + \gamma_F\frac{\gamma_{Ic} + w_{IcF}}{w_{FIc}}}(g(t) - \gamma_{Ib} n_{Ib})$$

$$= A(g(t) - \gamma_{Ib} n_{Ib}). \tag{14-17}$$

Where $A = \dfrac{1}{\gamma_{Ic} + \gamma_F\dfrac{\gamma_{Ic} + w_{IcF}}{w_{FIc}}}$.

From (14-15),

$$n_{Ib} = \frac{1}{\gamma_{Ib} + \gamma_F\frac{\gamma_{Ib} + w_{IbF}}{w_{FIb}}}(g(t) - \gamma_{Ic} n_{Ic})$$

$$= B(g(t) - \gamma_{Ic} n_{Ic}).$$

$$\tag{14-18}$$

Where, $B = \dfrac{1}{\gamma_{Ib} + \gamma_F\dfrac{\gamma_{Ib} + w_{IbF}}{w_{FIb}}}$.

Fig. 14-6 density of state of electrons in semiconductor

From (14-17)$\times B\gamma_{Ic}-$ (14-18),

$$n_{Ib} = Bg(t)\frac{A\gamma_{Ic} - 1}{A\gamma_{Ic}B\gamma_{Ib} - 1} = Bg(t)\frac{1 - A\gamma_{Ic}}{1 - A\gamma_{Ic}B\gamma_{Ib}}. \tag{14-19}$$

From (14-17)$-$Eq. (14-18)$\times A\gamma_{IIb}$,

$$n_{Ic} = Ag(t)\frac{B\gamma_{Ib} - 1}{A\gamma_{Ic}B\gamma_{Ib} - 1} = Ag(t)\frac{1 - B\gamma_{Ib}}{1 - A\gamma_{Ic}B\gamma_{Ib}}. \tag{14-20}$$

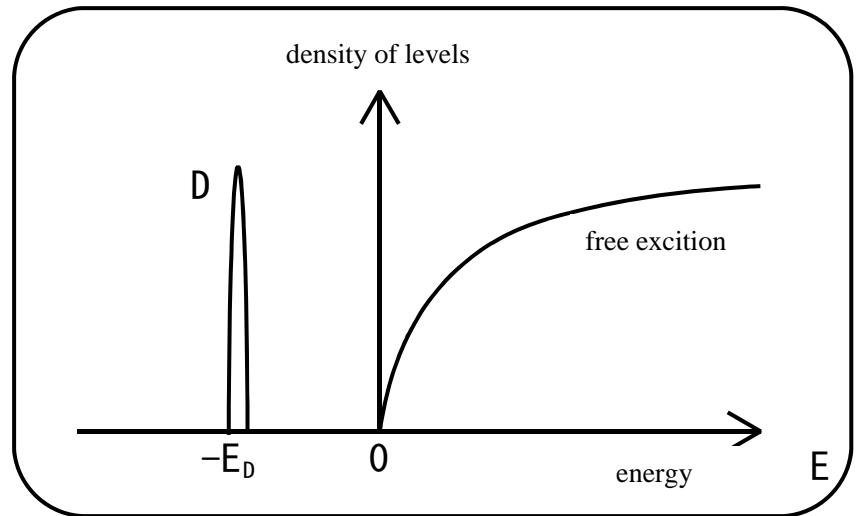Into eq. (14-12) , eqs. (14-19) and (14-20) are substituted,

$$\begin{aligned}
n_F &= \frac{g(t)}{\gamma_F} - \frac{1}{\gamma_F}(\gamma_{Ic}n_{Ic} + \gamma_{Ib}n_{Ib}) \\
&= \frac{g(t)}{\gamma_F} - \frac{\gamma_{Ic}(B\gamma_{Ib}-1)A + \gamma_{Ib}(A\gamma_{Ic}-1)B}{\gamma_F(AB\gamma_{Ic}\gamma_{Ib}-1)}g(t) \\
&= \frac{g(t)}{\gamma_F} \times \frac{A\gamma_{Ic} + B\gamma_{Ib} - AB\gamma_{Ic}\gamma_{Ib} - 1}{AB\gamma_{Ic}\gamma_{Ib} - 1} = \frac{g(t)}{\gamma_F} \times \frac{(1-A\gamma_{Ic})(1-B\gamma_{Ib})}{1-AB\gamma_{Ic}\gamma_{Ib}}.
\end{aligned} \tag{14-21}$$

Where, an intensity of the exciton luminescence is a product of the radiative recombination ratio of the free exciton and density of the free exciton, therefore the luminescence intensity of the free exction and I_c, I_b bound excitons are

$$PL_{FE} = \gamma_{Fr} \frac{g(t)}{\gamma_F} \times \frac{(1-A\gamma_{Ic})(1-B\gamma_{Ib})}{1-AB\gamma_{Ic}\gamma_{Ib}}, \tag{14-22}$$

$$PL_{Ic} = \gamma_{Icr} Ag(t)\frac{1-B\gamma_{Ib}}{1-AB\gamma_{Ic}\gamma_{Ib}}, \tag{14-23}$$

$$PL_{Ib} = \gamma_{Ibr} Bg(t)\frac{1-A\gamma_{Ic}}{1-AB\gamma_{Ic}\gamma_{Ib}}. \tag{14-24}$$

② deducing w_{FIi} and w_{IiF}

Now, let consider the w_{FIi} and w_{IiF}. Here i is b or c. It can be assumed that a ratio of rate w_{FIi} and w_{IiF} do not depend on γ_F and γ_{Ii} because this process is elementary step(a process only converting between bound exction and free exciton).

From in a case of detailed balance with $\gamma_F = 0$ and $_{Ii} = 0$ and eqs. (14-6) and (14-7),

$$w_{FIi}\left(1 - \frac{n_{Ii}}{N_{Ai}}\right)n_F = w_{IiF}n_{Ii}. \tag{14-25}$$

Here, let consider a distribution of electrons in a semiconductor, before considering distributions of free exciton and bound exciton (1).

In the case of that as shown in Fig. 14-6 levels a number of which is $N_D{}^0$ are overlapped at energy E_D and higher than energy 0 the electron is free, it is assumed that there are continuous levels which has density of state shown in eq. (14-26),

$$\frac{4\pi V}{h^3}\sqrt{2m^3 E}dE \quad (V: \text{volume of the semiconductor}, \; m: \text{weight of electron} \; h: \text{Planck constant}).$$
$$\tag{14-26}$$

The level of $-E_D$ is in the semiconductor and an electron is captured by an atom D. If the atom D is ionized and the electron can be move in the semiconductor, the electron occupies the level which energy is $E \geqq 0$. That is reaction equation is expressed as

$$D \underset{\rightarrow}{\overset{\leftarrow}{}} D^+ + \text{free electron}. \tag{14-27}$$

If it is assumed that a number of free electron is N_C and a number of electrons at level $-E_D$ is N_D, following is satisfied,

$$N_C + N_D = N = \text{a number of all electrons}. \tag{14-28}$$

The distribution of the electron is Fermi-Dirac distribution, therefore

$$N_D = \frac{N_D{}^0}{\exp\left(\dfrac{-E_D - \mu}{kT}\right) + 1}, \tag{14-29}$$

$$N_C = \sum_{E=0}^{\infty} \frac{1}{\exp\left(\dfrac{E - \mu}{kT}\right) + 1}. \tag{14-30}$$

where, μ is Fermi energy.

In this case, a number of all electrons N is not so large, that is $N_C \leqq N$, and the electrons can be dealt as Boltzman gas, therefore eq. (14-30) becomes

$$N_C = \frac{g_E}{g_D} \frac{(2\pi mkT)^{3/2}}{h^3} V \exp(\mu/kT), \tag{14-31}$$

where g_E and g_D are spin degeneracy of the free electron and the captured electron , respectively. From eq. (14-29)

$$\frac{N_D}{N_D{}^0 - N_D} = \exp\left(\frac{E_D}{kT} + \frac{\mu}{KT}\right). \tag{14-32}$$

From eqs. (14-31) and (14-32) μ is eliminated, and a number of the atom which lost electron is defined as $N_D{}^+$, that is

$$N_D{}^+ = N_D{}^0 - N_D, \tag{14-33}$$

therefore

$$\frac{N_D{}^+ N_C}{N_D} = \frac{g_E}{g_D} \frac{(2\pi mkT)^{3/2}}{h^3} V \exp(-E_D / kT). \tag{14-34}$$

N_D, $N_D{}^+$ and N_C per unit volume are defined as n_D, $n_D{}^+$ and n_C, respectively, and then

$$\frac{n_D{}^+ n_C}{n_D} = \frac{g_E}{g_D} \frac{(2\pi mkT)^{3/2}}{h^3} \exp(-E_D / kT). \tag{14-35}$$

The free exciton is constructed with an electron and a hole these are combined by Coulomb force, and the free exciton can move in crystal freely. On the other hand, the bound exciton is generated by connecting free exciton with an impurity or a lattice defect, and therefore the bound exciton cannot move in crystal freely. The exciton is Boson, but at low density, a distribution of the exciton can be dealt as Boltzman distribution.

From the above, the free exciton can be considered as same as the electron which can move in crystal freely, and the bound exciton can be considered as same as the electron which captured the atom D.

Here, we discuss the exciton again. It is assumed that in the condition of $\gamma_F = 0$ and $\gamma_{Ii} = 0$, the exciton systems are thermal equilibrium condition ($n_F + n_{Ii} = $ const) at temperature T. The atom D is considered as the bound exciton, the free electron is considered as free exciton, that is $n_C \to n_F$, $n_D \to n_{Ii}$, $n_D{}^0 \to N_{Ai}$, $E_D \to E_{Ii}$ (binding energy between free electron and captur center), $g_E \to g_F$ (degeneracy of spin of free exciton), $g_D \to g_{Ii}$ (degeneracy of spin of bound exciton), and if mass of the free exciton is assumed m, followings are satisfied,

$$n_F = \frac{g_F}{g_{Ii}} \frac{(2\pi mkT)^{3/2}}{h^3} e^{\mu/kT}, \tag{14-36}$$

$$\frac{n_{Ii}}{N_{Ai} - n_{Ii}} = e^{E_{Ii}/kT + \mu/kT}. \tag{14-37}$$

from eqs. (14-25), (14-36) and (14-37) a relation between w_{FIi} and w_{IiF} is

$$\frac{w_{\text{IiF}}}{w_{\text{FIi}}} = \frac{n_{\text{F}}\left(1 - \dfrac{n_{\text{Ii}}}{N_{\text{Ai}}}\right)}{n_{\text{Ii}}} = \frac{g_{\text{F}}}{g_{\text{Ii}}} \frac{(2\pi mkT)^{3/2}}{h^3 N_{\text{Ai}}} e^{-\frac{E_{\text{Ii}}}{kT}} . \tag{14-38}$$

A paper which discusses free and bound exciton in a GaAs/Al$_x$Ga$_{1-x}$As quantum well(2), a ratio is expressed as

$$\frac{w_{\text{BF}}}{w_{\text{FB}}} = \frac{g_{\text{F}}}{g_{\text{B}}} \frac{(2\pi mkT)^{2/2}}{h^2 N_{\text{A}}} e^{-\frac{E_{\text{B}}}{kT}} ,$$

where, the subscript of B corresponds the subscript of Ii. The quantum well is two dimensional, and the ratio mentioned above converts into three dimensional corresponds to (14-38). Therefore the eq. (14-38) is reasonable.

Next, a relation between w_{FIi} and collision cross-section σ_i, the cross-section is between one free exciton and one free exciton capture center. An average velocity of the free electron is assumed v, following is satisfied

$$w_{\text{FIi}} \approx \sigma_i N_{\text{Ai}} v , \tag{14-39}$$

where, i = c or b, and σ_i is a cross-section which related to bound exciton I$_i$. If the free exciton is distributed as Boltzman distribution, the average velocity of the free exciton is expressed as

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \;\text{から}\quad v = \sqrt{\frac{3kT}{m}} , \tag{14-40}$$

therefore w_{FIi} is expressed as

$$w_{\text{FIi}} = \sigma_i N_{\text{Ai}} v = \sigma_i N_{\text{Ai}} \left(\frac{3kT}{m}\right)^{1/2} . \tag{14-41}$$

From eqs. (14-38), (14-41),

$$\begin{aligned}
w_{\text{IiF}} &= \frac{g_{\text{F}}}{g_{\text{Ii}}} \frac{3^{1/2}(2\pi)^{3/2} m(kT)^2}{h^3} \sigma_i e^{-\frac{E_{\text{Ii}}}{kT}} \\
&= C_{\text{wi}} T^2 \sigma_i e^{-\frac{E_{\text{Ii}}}{kT}}
\end{aligned} \tag{14-42}$$

where

$$C_{\text{wi}} = \frac{g_{\text{F}}}{g_{\text{Ii}}} \frac{3^{1/2}(2\pi)^{3/2} mk^2}{h^3} .$$

③ life time of the bound exciton luminescence

After excitation by weak pulse $(n_{\text{Ii}} \ll N_{\text{Ai}})$,

$$\frac{dn_{\text{F}}}{dt} = -(w_{\text{FIc}} + w_{\text{FIb}} + \gamma_{\text{F}})n_{\text{F}} + w_{\text{IcF}}n_{\text{Ic}} + w_{\text{IbF}}n_{\text{Ib}}, \tag{14-43}$$

$$\frac{dn_{\text{Ic}}}{dt} = -(\gamma_{\text{Ic}} + w_{\text{IcF}})n_{\text{Ic}} + w_{\text{FIc}}n_{\text{F}}, \tag{14-44}$$

$$\frac{dn_{\text{Ib}}}{dt} = -(\gamma_{\text{Ib}} + w_{\text{IbF}})n_{\text{Ib}} + w_{\text{FIb}}n_{\text{F}}. \tag{14-45}$$

If parameters are substituted as $w_{\text{FIc}} + w_{\text{FIb}} + \gamma_{\text{F}} \to \gamma_{\text{F}}$, $w_{\text{IcF}} + \gamma_{\text{Ic}} \to \gamma_{\text{Ic}}$, $w_{\text{IbF}} + \gamma_{\text{Ib}} \to \gamma_{\text{Ib}}$, equations mentioned above are rewritten as

$$\frac{dn_{\text{F}}}{dt} = -\gamma_{\text{F}}n_{\text{F}} + w_{\text{IcF}}n_{\text{Ic}} + w_{\text{IbF}}n_{\text{Ib}}, \tag{14-46}$$

$$\frac{dn_{Ic}}{dt} = -\gamma_{Ic}n_{Ic} + w_{FIc}n_F, \tag{14-47}$$

$$\frac{dn_{Ib}}{dt} = -\gamma_{Ib}n_{Ib} + w_{FIb}n_F. \tag{14-48}$$

From eqs. (14-46) and (14-47), (it is defined as $\dot{n} = dn/dt$, $\ddot{n} = d^2n/dt^2$)

$$\frac{\ddot{n}_{Ic} + \gamma_{Ic}\dot{n}_{Ic}}{w_{FIc}} = -\gamma_F \frac{\dot{n}_{Ic} + \gamma_{Ic}n_{Ic}}{w_{FIc}} + w_{IcF}n_{Ic} + w_{IbF}n_{Ib},$$

$$\ddot{n}_{Ic} + (\gamma_{Ic} + \gamma_F)\dot{n}_{Ic} + (\gamma_F\gamma_{Ic} - w_{FIc}w_{IcF})n_{Ic} = w_{FIc}w_{IbF}n_{Ib}.$$

If it is assumed that $\alpha_1 = \gamma_{Ic} + \gamma_F$, $\alpha_2 = \gamma_F\gamma_{Ic} - w_{FIc}w_{IcF}$, $\alpha_3 = w_{FIc}w_{IbF}$,

$$\ddot{n}_{Ic} + \alpha_1\dot{n}_{Ic} + \alpha_2 n_{Ic} = \alpha_3 n_{Ib}. \tag{14-49}$$

From eqs. (14-46) and (14-48),

$$\ddot{n}_{Ib} + (\gamma_{Ib} + \gamma_F)\dot{n}_{Ib} + (\gamma_F\gamma_{Ib} - w_{FIb}w_{IbF})n_{Ib} = w_{FIb}w_{IcF}n_{Ic}.$$

It is assumed that $\beta_1 = \gamma_{Ib} + \gamma_F$, $\beta_2 = \gamma_F\gamma_{Ib} - w_{FIb}w_{IbF}$, $\beta_3 = w_{FIb}w_{IcF}$,

$$\ddot{n}_{Ib} + \beta_1\dot{n}_{Ib} + \beta_2 n_{Ib} = \beta_3 n_{Ic}. \tag{14-50}$$

Where, it is assumed that $n_{Ic} = A\exp(-\lambda_{Ic}t)$, $n_{Ib} = B\exp(-\lambda_{Ib}t)$,

$$(\lambda_{Ic}^2 - \alpha_1\lambda_{Ic} + \alpha_2)A\exp(-\lambda_{Ic}t) = \alpha_3 B\exp(-\lambda_{Ib}t), \tag{14-51}$$

$$(\lambda_{Ib}^2 - \beta_1\lambda_{Ib} + \beta_2)B\exp(-\lambda_{Ib}t) = \beta_3 A\exp(-\lambda_{Ic}t). \tag{14-52}$$

From sum of eqs (14-51) and (14-52),

$$(\lambda_{Ic}^2 - \alpha_1\lambda_{Ic} + \alpha_2 - \beta_3)A\exp(-\lambda_{Ic}t) + (\lambda_{Ib}^2 - \beta_1\lambda_{Ib} + \beta_2 - \alpha_3)B\exp(-\lambda_{Ib}t) = 0. \tag{14-53}$$

To satisfy eq. (14-53), following must be satisfied,

$$\lambda_{Ic}^2 - \alpha_1\lambda_{Ic} + \alpha_2 - \beta_3 = 0, \quad \lambda_{Ib}^2 - \beta_1\lambda_{Ib} + \beta_2 - \alpha_3 = 0.$$

From $\lambda_{Ic}^2 - \alpha_1\lambda_{Ic} + \alpha_2 - \beta_3 = 0$,

$$\lambda_{Ic} = \frac{a_1 \pm \sqrt{\alpha_1^2 - 4(\alpha_2 - \beta_3)}}{2}$$

$$= \frac{(\gamma_{Ic} + \gamma_F) \pm \sqrt{(\gamma_{Ic} + \gamma_F)^2 - 4(\gamma_F\gamma_{Ic} - w_{FIc}w_{IcF} - w_{FIb}w_{IcF})}}{2}$$

$$= \frac{(\gamma_{Ic} + \gamma_F) \pm \sqrt{(\gamma_{Ic} - \gamma_F)^2 + 4(w_{FIc}w_{IcF} + w_{FIb}w_{IcF})}}{2}.$$

where, the rewritten parameters are returned to original of $w_{FIc} + w_{FIb} + \gamma_F \rightarrow \gamma_F$, $w_{IcF} + \gamma_{Ic} \rightarrow \gamma_{Ic}$, $w_{IbF} + \gamma_{Ib} \rightarrow \gamma_{Ib}$, above equation is rewritten as

$$\lambda_{Ic} = \frac{(w_{IcF} + \gamma_{Ic} + w_{FIc} + w_{FIb}\gamma_F)}{2}$$

$$\pm \frac{\sqrt{(w_{IcF} + \gamma_{Ic} - \gamma_F - w_{FIc} - w_{FIb})^2 + 4(w_{FIc}w_{IcF} + w_{FIb}w_{IcF})}}{2}. \tag{14-54}$$

In this chapter, the example of the observation is carried out very low temperature ($w_{IiF} \approx 0$) and the observed decay curve of the bound exciton luminescence is a slow decay components, that is the decay curve is observed after ~10ps of excitation. For the example of the observation, life time of the free exciton is shorter than 5 ps. Therefore almost of the free excitons are annihilated and $\gamma_F \gg \gamma_{Ii}$, w_{FIi}, w_{IiF}.

From the above and eq. (14-54),

$$\lambda_{Ic} \approx \frac{(w_{IcF} + \gamma_{Ic} + w_{FIc} + w_{FIb} + \gamma_F) - \sqrt{(\gamma_{Ic} + w_{IcF} - \gamma_F - w_{FIc} - w_{FIb})^2}}{2}$$

$$= \frac{(w_{IcF} + \gamma_{Ic} + w_{FIc} + w_{FIb} + \gamma_F) - (-\gamma_{Ic} - w_{IcF} + \gamma_F + w_{FIc} + w_{FIb})}{2}$$

$$= \gamma_{Ic} + w_{IcF}.$$

Therefore, τ_{Ic} which is a life time of the bound exction I_c is expressed as

$$\tau_{Ic} = \frac{1}{\gamma_{Ic} + w_{IcF}} = \frac{1}{\gamma_{Icr} + \gamma_{Icnr} + w_{IcF}} = \frac{1}{\gamma_{Icr} + \gamma_{Icnr} + C_{wc}\sigma_c T^2 e^{-\frac{E_{Ic}}{kT}}}. \qquad (14\text{-}55)$$

As same as above, from $\lambda_{Ib}^2 - \beta_1 \lambda_{Ib} + \beta_2 - \alpha_3 = 0$, τ_{Ib} which is a life time of the bound exciton I_b is expressed as

$$\tau_{Ib} = \frac{1}{\gamma_{Ib} + w_{IbF}} = \frac{1}{\gamma_{Ibr} + \gamma_{Ibnr} + w_{IbF}} = \frac{1}{\gamma_{Ibr} + \gamma_{Ibnr} + C_{wb}\sigma_b T^2 e^{-\frac{E_{Ib}}{kT}}}. \qquad (14\text{-}56)$$

④ estimation of the capture cross-section of the free exciton capture center σ_i by fitting

A temperature dependence of the bound exciton life times estimated from Fig. 14-4 are shown in Fig. 14-7. The capture cross-section of the free exciton capture center σ_i can be estimated by fitting of eqs. (14-55) and (14-56) to Fig. 14-7. To fit the eqs. (14-55) and '14-56) to Fig. 14-7, values of γ_{Iir} and γ_{Iinr} are necessary. As shown in Fig. 14-7, at low temperature, the life time of the bound exciton is almost constant. However, at higher than 30 K of the sample temperature , the life time of the bound exciton luminescence decrease. The reason is that since the binding energy of the bound exciton is about one third of CuGaS$_2$ LO phonon energy, as shown by w_{IiF} the bind between the bound exciton and capture center is cut. Therefore in the region of the temperature from 30 K to 100K, $\gamma_{Iinr} \ll w_{IiF}$ is satisfied.

Here, in the observation of this chapter, luminescence life time at low temperature is assumed radiative recombination life time of the bound exciton, that is, it is assumed that $\tau_{Iir} = \gamma_{Iir}^{-1}$. From fig. 14-7 the life times are estimated as $\tau_{Icr} = 143$ ps and $\tau_{Ibr} = 123$ ps.

Here, from the reason mentioned as follows, at $T = 0$ it is assumed that $\gamma_{Iinr} \ll \gamma_{Iir}$ is satisfied.

① at low temperature, the life time of the bound exciton is almost constant and the life time almost does not depend on temperature, and interaction of exciton and phonon are very little.

② Auger recombination process which does not depend on thermal energy is not dominated process in the CuGaS$_2$. The reason is
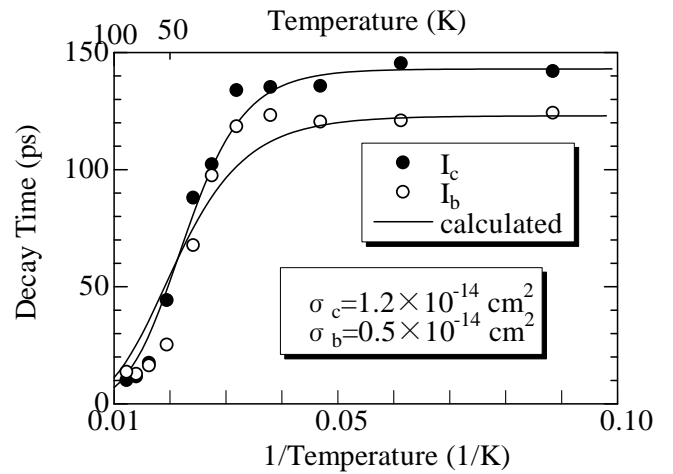

Fig. 14-7 temperature dependence of life time of the bound exciton luminescence

described as follows. There is no report on the Auger recombination of CuGaS$_2$ bound exciton and non-radiative life time of the CuGaS$_2$ bound exciton by the Auger recombination process is unknown. For CdS, there is a report of that and the life time of the Auger recombination process is the order of the 10 ns. Here, optical properties of CuGaS$_2$ resembles to that of CdS, and CdS is often compared with CuGaS$_2$. If the life time by the Auger recombination process is as same as that of CdS, the life time of the observation in this chapter is ~100 ps and this is very short than 10 ns. Therefore, for CuGaS2, the Auger recombination process can be neglected.

From the reasons mentioned above, at T ~ 0K, it is assumed that $\gamma_{\text{linr}} \ll \gamma_{\text{lir}}$. Therefore it is assumed that at 10 ~ 100 K, γ_{linr} can be neglected.

Fitting results are shown in Fig. 14-7 as ● for (Ic) and as ○ for (Ib). Here, at the fitting, binding energies of the bound excitons are estimated from separated spectrum, E_{Ic}=2.501 eV－2.492 eV＝9 meV, E_{Ib}=2.501 eV－2.495 eV＝6 me. Other parameters are assumed that $g_{\text{F}} / g_{\text{Ii}} = 4 / 2 = 2$ and $m = m_{\text{e}} + m_{\text{h}} = 0.26m_0 + 0.69m_0$ [13], where m, m_{e} and m_{h} are reduced masses of the free exciton, the electron and the hole, respectively.

As shown in Fig. 14-7, experimental results and fitting are almost same. From the fitting, capture cross-section of free exciton capture center are $\sigma_{\text{c}} = 2.9 \times 10^{-14}\,\text{cm}^2$ and $\sigma_{\text{b}} = 1.4 \times 10^{-14}\,\text{cm}^2$, respectively. These values are reasonable because these values are same order of the radius of CuGaS$_2$ exciton（～10 Å order）[3] and the cross-section of different sample (CGS09 and CGS10) show same order.

The obtained values are compared with that of other semiconductors. In ref. (7), for GaTe and GaSe, the time resolved exciton spectrum was analyzed by rate equation, and free exciton capture cross-section were estimated. The cross-section of GaTe and GaSw are $1.2 \times 10^{-14}\text{cm}^2$ and $0.4 \times 10^{-14}\text{cm}^2$, respectively and these values are same order of the cross-section of CuGaS$_2$

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