Chapter 11.

Optical Processes and Excitons

$\varepsilon(\omega, k)$: electromagnetic field에 대한 반응

이것은 electronic band structure에 매우 senstive 하다.

$$\varepsilon = \varepsilon' + i\varepsilon''$$

Directly accessible function : R(w) , n(w) , k(w)

extinction coefficient

refractive index

reflectance

Optical reflectance

$$\frac{E(refl)}{E(inc)} \equiv r(\omega) \equiv \rho(\omega)\exp[i\theta(\omega)]$$ *reflective coefficient*라 불리운다.

$$r(\omega) = \frac{n+ik-1}{n+ik+1}$$

definition n(w) and k(w) are related

$$\sqrt{\varepsilon(\omega)} \equiv n(\omega) + ik(\omega)$$
$$\equiv N(\omega)$$

$$E_y(inc) = E_{y_0}\exp[i(kx - \omega t)]$$

$$E_y(trans) \propto \exp[i(n+ik)kx - \omega t]$$
$$= \exp[-k\,kx]\exp[i(nkx - \omega t)]$$

Reflectance R

$$R = E^*(refl)E(refl) / E^*(inc)E(inc)$$
$$= r^* r$$
$$= \rho^2 \qquad \rho = |r|$$

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$
$$= (n+ik)^2$$
$$= n^2 - k^2 + 2nki$$

Kramers -Kronig Relations

Real을 알면 imaginary를 알 수 있고 imaginary를 알면 real을 알 수 있다.

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega) \quad \textit{Responsefunction}$$

$$X_\omega = \alpha(\omega)F_\omega$$

equation of motion

$$\sum_j M_j\left(\frac{d^2}{dt^2} + p_i\frac{d}{dt} + \omega_j^2\right)X = F$$

$$\therefore \sum_j M_j(-\omega^2 - i\omega p_j + \omega_j^2)X_\omega = F_\omega$$

$$X = \int X_\omega \exp[-i\omega t]dt \qquad F = \int F_\omega \exp[-i\omega t]\, dt$$

$$\therefore \quad \alpha(\omega) = \sum_j \frac{1}{M_j(-\omega^2 - i\omega p_j + \omega_j^2)}$$

$$= \sum_j \frac{f_j(-\omega^2 + i\omega p_j + \omega_j^2)}{(-\omega^2 - i\omega p_j + \omega_j^2)(-\omega^2 + i\omega p_j + \omega_j^2)}$$

$$= \sum f_j \frac{(\omega_j^2 - \omega^2 + i\omega p_j)}{(\omega_j^2 - \omega^2)^2 + \omega^2 p_j^2}$$

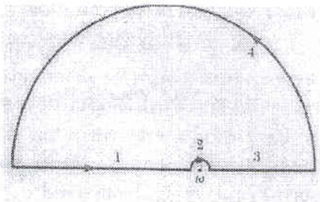
f_j:

all positive for a passive system

p_j: *relation frequency*

Kramers - Kronig relation

(1) The poles of $\alpha(\omega)$ are all below the real axis



(2) $\frac{\alpha(\omega)}{\omega}$ ---------→ vanish

(3) $\alpha'(\omega)$ *is even*

α'' *is odd*

$$\alpha(\omega) = \frac{1}{\pi i} p\int_{-\infty}^{\infty} \frac{\alpha(s)}{s-\omega} ds$$

$$\alpha'(\omega) = \frac{1}{\pi} p\int_{-\infty}^{\infty} \frac{\alpha''(s)}{s-\omega} ds$$

$$= \frac{1}{\pi} p\left[\int_0^{\infty} \frac{\alpha''(s)}{s-\omega} ds + \int_{-\infty}^{0} \frac{\alpha''(p)}{p-\omega} dp\right]$$

$$= \frac{1}{\pi} p\left[\int_0^{\infty} \frac{\alpha''(s)}{s-\omega} ds + \int_{\infty}^{0} \frac{\alpha''(-s)}{-s-\omega} d(-s)\right] \qquad \int_\infty^0 \frac{-\alpha''(s)}{s+\omega} ds$$

$$= \frac{1}{\pi} p\left[\int_0^{\infty} \frac{\alpha''(s)}{s-\omega} ds + \int_0^{\infty} \frac{\alpha''(s)}{s+\omega} ds\right]$$

$$= \frac{1}{\pi} p\int_0^{\infty} \frac{2s\alpha''(s)}{s^2-\omega^2} ds$$

$$\alpha'(\omega) = \frac{2}{\pi} p\int_0^{\infty} \frac{s\alpha''(s)}{s^2-\omega^2} ds$$

$$\alpha''(\omega) = -\frac{1}{\pi} p \int_{-\infty}^{\infty} \frac{\alpha'(s)\,ds}{s-\omega}$$
$$= -\frac{2\omega}{\pi} p \int_{0}^{\infty} \frac{\alpha'(s)ds}{s^2-\omega^2}$$

Kramers - Kronig Relation 을 적용하자.

$$\ln r(\omega) = \ln R^{\frac{1}{2}}(\omega) + i\theta(\omega)$$

$$\theta(\omega) = -\frac{\omega}{\pi} p \int_0^{\infty} \frac{\ln R(s)}{s^2-\omega^2} ds$$

$$\frac{1}{s^2-\omega^2} = \frac{1}{(s-\omega)(s+\omega)}$$

$$= -\frac{1}{2\pi} p \int_0^{\infty} \ln\left|\frac{s-\omega}{s+\omega}\right| \frac{d\ln R(s)}{ds} ds$$

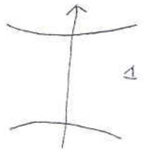
$$= \left(\frac{1}{s-\omega} - \frac{1}{s+\omega}\right)\frac{1}{2\omega}$$

Mathematical note

$$\alpha(\omega) = \sum_j \frac{(\omega_j^2-\omega^2) + i\omega p_j}{(\omega_j^2-\omega^2) + \omega^2 P_j^2}$$

Electronic

Interband transition



1.이렇게 gap보다 더 크면 optical spectroscopy는 broad feature만 보인다.

direct interband absorption은 $\hbar w = \varepsilon_c(\vec{k}) - \varepsilon_v(\vec{k})$.

Excitons

bound electron - hole pair를 exciton이라 한다.

exciton이 crystal에서 움직이면서 에너지를 전달하다.

전기는 전달 안 함

Exciton은 모든 insulating crystal에서 forming 될 수 있다.

gap이 indirect이면 unstable 하다.

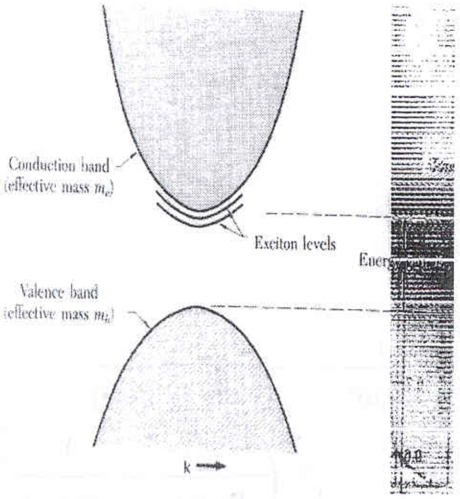
모든 exciton이 다 unstable하다. - 전자가 hole로 들어간다.

threshold of this process

$\hbar\omega > E_g$ in a direct process

$\hbar\omega > E_g - \hbar\Omega$ indirect process

정확하게는 exciton의 binding 에너지를 고려하야 한다.

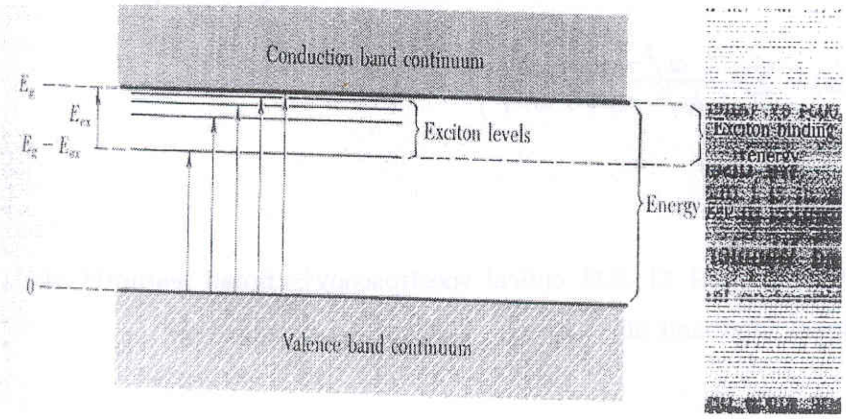


binding energy :

1. exciton을 만드는 에너지와 free electron, free hole을 만드는 에너지의 차이
2. recombination lumunescence , free electron - hole combination
3. photo - ionization of excitons

⇒ exciton is weakly bounded: Mott and Wannier

⇒ tightly bounded : Frenkel



Frenkel Excitons

Tightly bound.

⇒ hole은 바로 옆에 있다.(single atom에 있다.)

⇒ 이 exciton이 hopping을 한다.

⇒ Crystalline inert gas : Frenkel model로 설명

Atomic crypton : lowest strong atomic transition at 9.99eV

Crystal crypton : 10.2 ~~11.7~~eV (gap) 이 11.7

원자 Crypton 9.99eV

결정내에서는 10.2eV

exciton의 ground state energy

11.7-10.2 = 1.5 eV(exciton의 ground state energy)

Exciton의 propagation

옆으로 옆으로 wave propagation

$$\Psi_g = u_1 u_2 \circ \circ \circ u_{N-1} u_N$$

single atom이 excited 되어 있다.

$$\varphi_j = u_1 u_2 \circ \circ \circ u_{j-1} u_j u_{j+1} \circ \circ \circ u_N$$

$$H\varphi_j = \varepsilon\varphi_j + T(\varphi_{j-1} + \varphi_{j+1})$$

propagate 한다.

ε : *free atom excitation energy*

T : *excition* $j \dashrightarrow j-1$

$j \dashrightarrow j+1$

이 solution은 wave 모양이다.

$$\Psi_k = \sum \exp[ijka]\varphi_j$$

$$H\Psi_k = \sum_j \exp[ijka]\, H\varphi_j$$

$$= \sum_j \exp[ijka]\ \ [\varepsilon\varphi_j + T(\varphi_{j-1} + \varphi_{j+1})]$$

rearrange 하자

$$H\Psi_k = \sum \exp[ijka]\,[\varepsilon + T(\exp[ika] + \exp[-ika])]\ \varphi_j$$

$$= [\varepsilon + 2T \cdot \cos ka]\ \Psi_k$$

$$E_k = \varepsilon + 2T\cos ka$$

periodic boundary condition

$$K = \frac{2\pi s}{Na} \qquad s = -\frac{1}{2}N, -\frac{N}{2}+1, \cdots, \frac{1}{2}N-1$$

Alkali Halide : localzed exciton on the negative halogen ion

visible 에서는 exciton 안 보임 transparent

UV에서 exciton 보이고

Molecular crystals :

Van der Waals binding between molecules

covalent 가 매우 강하다.

이러한 exciton은 Frenkel excitons

Weakly bound (Mott - Wannier)

$$U(r) = -\frac{e^2}{\varepsilon_r}$$

에너지가 cond. 보다 아래에서 bound state 있다.

$$E_n = E_g - \frac{\mu e^4}{2\hbar^2\varepsilon^2 n^2}$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

예 Cu_2O $\qquad v(cm^{-1}) = 17508 - \frac{800}{n^2}$

Exciton Condensation into Electron - Hole drop

electron - hole drop 이 Ge 속에서 생긴다.

$\hbar\omega > E_g$ 이면 free - electron and free hole이 생긴다.

recombination $8\mu s$

electron - hole recombination and annihilation

$8\mu s$

만약 exciton concentration이 high이면 drop의 life time은 $40\mu s$

strained germanium $600\mu s$

excitons의 drop은 degenerated Fermi gas가 되고 metallic properties가 나타난다.

Raman effect

Photon inelatically scatter

creation or annihilation of a phonon or magnon

Selection rule

$$\omega = \omega' \pm \Omega \ ; \quad k = k' \pm K$$

Ω, K : phonon의 creation 또는 annihilation

2nd order Raman effect :

two phonons are involved in the inelastic scattering of photon

strain dependence of electronic polarizability

$$\alpha = \alpha_0 + \alpha_1 u + \alpha_2 u^2 + \circ \circ \circ$$

α_1 : phonon amplitude

$$u(t) = u_0 \cos \Omega t$$

induced electric dipole moment

$$\alpha_1 E \cdot u$$

$$= \alpha_1 E_0 \ u_0 \cos \omega t \ \cos \Omega t$$

$$= \frac{1}{2} \alpha_1 E_0 u_0 \ [\cos(\omega + \Omega)t + \cos(\omega - \Omega)t]$$

$\omega - \Omega$: stokes line

$\omega + \Omega$: anti stokes line

$$I(\omega - \Omega) \propto |\langle n_{K+1} | u | n_K \rangle|^2 \propto n_K + 1$$

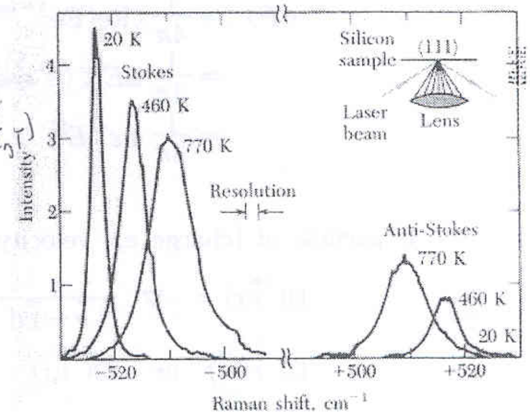
$$I(\omega + \Omega) \propto |\langle n_{K-1} | u | n_K \rangle|^2 \propto n_K$$

Population

$$\frac{I(\omega + \Omega)}{I(\omega - \Omega)} = \frac{\langle n_K \rangle}{\langle n_K \rangle + 1} = \exp[-\hbar\Omega / k_B T]$$

$$\because \quad \langle n_K \rangle = \frac{1}{\exp[\hbar\omega/k_B T]-1}$$

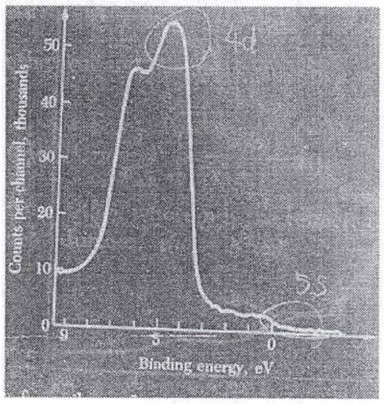
$$\langle n_K + 1 \rangle = \frac{1+\exp()-1}{\exp()-1} = \frac{\exp(\hbar\omega/k_B T)}{\exp()-1}$$



Electron Spectroscopy with X-ray

X-ray Photoemission from solids (XPS)
Ultraviolet Photoemission (UPS)

Density of state($D(\varepsilon)$)
photon이 incident photon - binding energy = K.E.
전자는 50Å 정도 나올 수 있다.
ESCA : resolution 0.6 eV
Electron Spectroscopy for Chemical Analysis
valence structure of silver =>그림



Excitation
99.2 eV binding energy
117 eV에서 또 보인다.
single palsmon excitation
134.7 eV : double plasmon excitation

Energy loss of fast particles in a solid
전자를 빛 대신쓰자.
$Im\{\varepsilon(\omega)\}$: energy loss by an electromagnetic wave in a solid
$Im\{\frac{1}{\varepsilon(\omega)}\}$: energy loss by a charged particle that penetrated a solid

$$P = \frac{1}{4\pi} E \frac{\partial D}{\partial t} \qquad E = E_0 e^{(-iwt)}$$
$$= \left[\frac{1}{4\pi} E \cdot (-iw)\right] \cdot [\varepsilon(w) E e^{(-iwt)}] \qquad D = D_0 e^{(-iwt)}$$

$$-i\omega(\varepsilon'+i\varepsilon'')(\cos\omega t + i\sin\omega t)$$

$$= -i\omega\left[(\varepsilon'\cos\omega t - \varepsilon''\sin\omega t) + i(\varepsilon'\sin\omega t + \varepsilon''\cos\omega t)\right]$$

$$\begin{aligned}\langle P\rangle &= \frac{1}{4\pi}\langle \mathrm{Re}\{\mathrm{Ee}^{(-\mathrm{iwt})}\}\cdot \mathrm{Re}\{-\mathrm{iwDe}^{(-\mathrm{iwt})}\}\rangle \\ &= \frac{1}{4\pi}\,\omega E^2\langle(\varepsilon'\overset{\sin}{\ }wt + \varepsilon''\overset{\cos}{\ }wt)\cos wt\rangle \\ &= \frac{1}{8\pi}\,\omega\varepsilon'' E^2\end{aligned}$$

If particle of [charge e, velocity v] enters a crystal:

$$D(\vec{r},t) = -\nabla\frac{e}{|\vec{r}-\vec{v}t|}$$

$$D(\vec{r},\omega) \quad \text{or} \quad D(\vec{r},t)$$

$$E(\omega,\vec{k}) = D(\omega,\vec{k})\,/\,\varepsilon(\omega,\vec{k})$$

Time average power dissipation

$$P(\omega,\vec{k}) = \frac{1}{4\pi}<\{\mathrm{Re}\frac{D(\omega,k)}{\varepsilon(\omega,k)}\quad e^{-i\omega t}\}\cdot\mathrm{Re}\{-i\omega D(\omega,k)\ e^{-i\omega t}\}$$

$$= \frac{1}{4\pi}\,\omega D^2(\omega,k) < [\left(\frac{1}{\varepsilon}\right)'\cos\omega t + \left(\frac{1}{\varepsilon}\right)''\sin\omega t][-\sin\omega t] >$$

Whence

$$P(\omega,\vec{k}) = \frac{-1}{8\pi}\,\omega\left(\frac{1}{\varepsilon}\right)'' D^2(\omega,\vec{k})$$

$$= \frac{1}{8\pi}\,\omega\,\frac{\varepsilon''(\omega,k)}{|\varepsilon|^2}\,D^2(\omega,\vec{k})$$

energy loss function $\propto \mathrm{Im}\left(\frac{1}{\varepsilon(\omega,k)}\right)$

위 $P(\omega,k)$가 k에 무관하면

$$P(\omega) = -\frac{2}{\pi}\cdot\frac{e^2}{\hbar v}\,\mathrm{Im}\{\frac{1}{\varepsilon}\}\,\ln\left(\frac{k_0 v}{\omega}\right)$$