Chart of the Electromagnetic Spectrum

Size reference

man's height · paperclip thickness · cells · viruses · atom

football field · baseball · paper thickness · bacteria · water molecule · subatomic particles →

wavelength λ (m)

				1 ft	1 cm	1 mm		1 mil	1 μ				1 nm	1 Å		1 pm
10^3	10^2	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}

wavenumber (cm⁻¹)

10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5	10^6	10^7	10^8	10^9	10^{10}

electron volt (eV)

10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5	10^6

frequency (Hz)

	1 MHz				1 GHz				1 THz			1 PHz		1 EHz			1 ZHz
10^5	10^6	10^7	10^8	10^9	10^{10}	10^{11}	10^{12}	10^{13}	10^{14}	10^{15}	10^{16}	10^{17}	10^{18}	10^{19}	10^{20}	10^{21}

Bands

Radio Spectrum · Terahertz · Infrared · Ultraviolet · X-ray · Gamma

Broadcast and Wireless · Microwave · Far IR · Mid IR · Near IR · Near UV · Extreme UV · Soft X-ray · Hard X-ray

electronics · optics

Visible wavelengths (nm)

700 · 625 · 575 · 540 · 470 · 440

1.7 eV · 3.1 eV

Sources and Uses of Frequency Bands

- Sound Waves ← 20Hz-10kHz
- AM radio 600kHz-1.6MHz
- Ultrasound 1-20 MHz
- FM radio 88-108 MHz
- TV Broadcast 54-700 MHz
- Mobile Phones 900MHz-2.4GHz
- Wireless Data ~ 2.4 GHz
- Microwave Oven 2.4 GHz
- Radar 1-100 GHz
- Bio imaging 1-10 THz
- Screening 0.2-4.0 THz
- "mm wave" "sub-mm"
- Fiber telecom 0.7-1.4 μ
- Visible Light 425-750THz 700-400nm
- Remotes 850 nm
- Night Vision 10-0.7 μ
- Dental Curing 200-350nm
- Suntan 400-290nm
- Medical X-rays 10-0.1 Å
- Baggage screen 10-1.0 Å
- Crystallography 2.2-0.7 Å
- Cosmic ray observations <<1 Å
- PET imaging 0.1-0.01 Å

Communication

Display Business

Positron emission tomography

Diffraction

$$\lambda = 3\times10^8/\text{freq} = 1/(\text{wn}*100) = 1.24\times10^{-6}/\text{eV}$$

SURA Southeastern Universities Research Association ®

4. Optical Properties

4A. Maxwell's Equations and Light Propagation in Continuous Media
4B. Classical Model of Materials Response
4C. Quantum Phenomena: Absorption
4D. Quantum Phenomena: Luminescence

The optical properties are essentially **light-matter interactions** – how the light interacts and exchanges energies with matters. The main driving force is the **electric field** in the light that gives rise to the motion of electron and ions inside the matter. Therefore, there are three key players in the optical properties: **light, electron, and ion** (or to be more precise, ionic vibration). They can be treated classically or quantum mechanically depending on how we deal with the energy quantization. We will first start with the simple classical theory, and extend the theory to include quantum effects.

References
Bube Chap. 8
Griffith "Electrodynamics"
Fox "Optical Properties of Solids"
Kasap "Electronic Materials and Devices"

4A. Maxwell's Equations and Light Propagation in Continuous Media

4A.1. Maxwell's Equations in Media
4A.2. Light Propagation in Dielectric Media
4A.3. Optical Absorption in Dissipative Media

Maxwell's equations with charge and current sources (**cgs units**)

$$\nabla \cdot \vec{D} = 4\pi\rho$$

$$\nabla \cdot \vec{B} = 0$$

$$\nabla \times \vec{H} = \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

This is called microscopic version of Maxwell's equations. Within the material, one can still apply this form of Maxwell's equation by treating all the ions and electrons explicitly. However, this is unnecessarily complicated because we are mostly interested in macroscopic fields (with atomic details washed out). In this case, a more convenient approach is to describe the response of materials in terms of **continuous polarization and magnetization**. In fact, historically, the electromagnetism was developed long before the advent of atomic theory. Being ignorant of atomistic picture, the continuous media was the best concept that they can imagine. In the following chapters, we will introduce these four Maxwell's equations one by one, and describe how the equation changes within the theory of continuous media.

Maxwell's Equations

$$\nabla \cdot \vec{D} = 4\pi\rho$$

$$\nabla \cdot \vec{B} = 0$$

$$\nabla \times \vec{H} = \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$

$$\vec{H} = \vec{B} - 4\pi\vec{M}$$

$$\vec{D} = \epsilon\vec{E} \quad \textbf{dielectric constant}$$

$$\vec{P} = x_e\vec{E} \quad \textbf{electric susceptibility}$$

$$\vec{B} = \mu\vec{H} \quad \textbf{magnetic permeability}$$

$$\vec{M} = x_m\vec{H} \quad \textbf{magnetic susceptibility}$$

4A.1. Maxwell's Equations in Media

$$\nabla \cdot \vec{D} = 4\pi\rho$$

| **Maxwell's First Equation: Gauss Law** |

$$\vec{D} = \epsilon\vec{E}$$

When there is a point charge q at $\mathbf{r}'$, the electric field at $\mathbf{r}$ is given as follows:
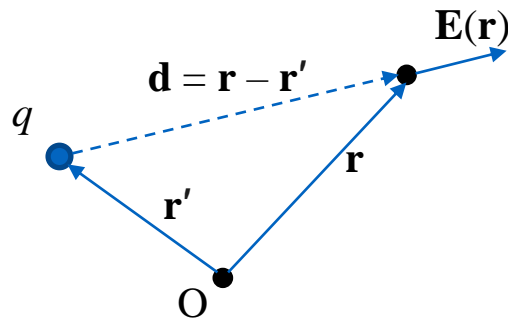
$$\mathbf{E}(\mathbf{r}) = \frac{q}{4\pi\epsilon_0 d^2}\hat{\mathbf{d}} \quad d = |\mathbf{r} - \mathbf{r}'|$$

When we put a charge Q at $\mathbf{r}$, the force experiences a force of $Q\mathbf{E}$.

When there are multiple point charges as in the right, the electric field is a vector sum of electric fields from each charge.

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\sum_i \frac{q_i}{4\pi\epsilon_0 d_i^2}\hat{\mathbf{d}}_i$$
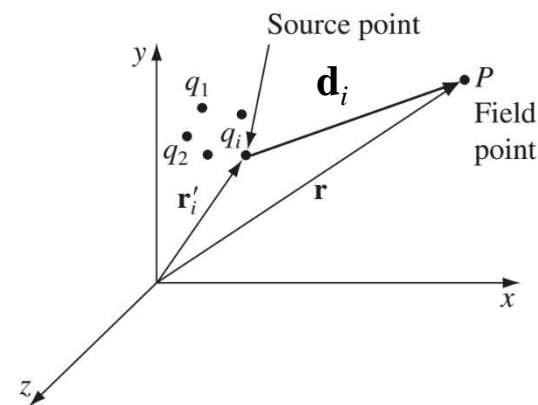
More generally, for **continuous distribution of charge density ρ(r)** ,

$$\mathbf{E}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0 d'^2}\hat{\mathbf{d}}' dV'$$

$$\rho(r)$$
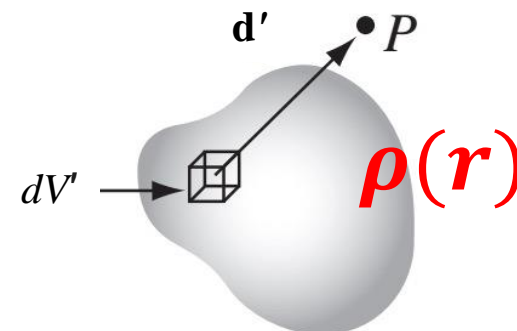
The Gauss'law is a consequence of $1/r^2$ dependence of electrical force. It states that

$$\oint_S \mathbf{E} \times d\mathbf{S} = \frac{1}{e_0} Q_{enc} = \frac{1}{e_0} \oint_V r(\mathbf{r}) dV$$

where Q_{enc} is the total charge inside the volume V that is enclosed by the surface S.

This is an integral version of Gauss's law. In order to change it into the differential form, we apply the divergence theorem for E field.

$$\int_S \mathbf{E} \cdot d\mathbf{S} = \int_V \nabla \cdot \mathbf{E} \, dV$$

Therefore, $\quad \int_V \nabla \cdot \mathbf{E} \, dV = \frac{1}{e_0} \int_V r(\mathbf{r}) dV$

Since the relation holds for any volume,

$$\nabla \cdot \vec{D} = 4\pi\rho \qquad \vec{D} = \epsilon \vec{E}$$

This is Gauss' law in differential form.
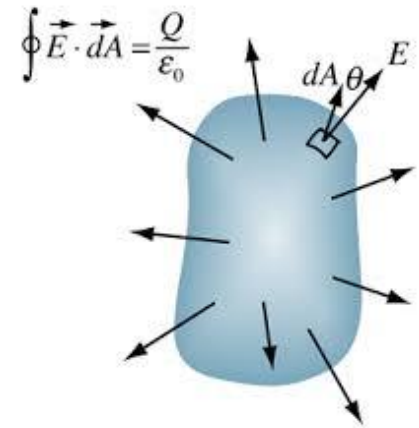
Now we consider electric fields inside the matter. The medium can include units that are **polarized** and produce **induced dipole moments** under electric fields E. (The electric fields also give rise to currents which generates B fields.) There several microscopic origins that contribute to the induced dipole moment and the following figure shows the electronic polarization.
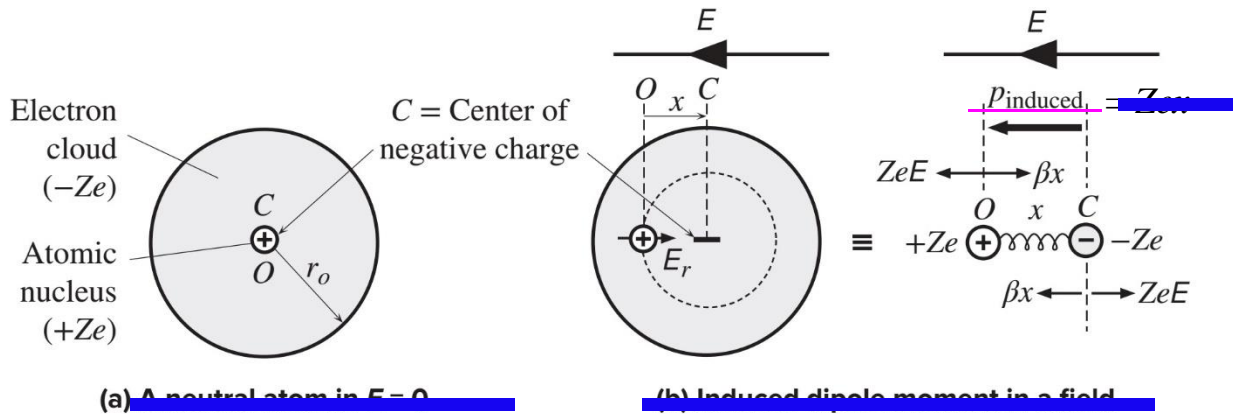
Here we assume that the medium is homogeneous and isotropic. If there are N polarizable units in a certain volume V and each unit has **dipole moments of p_i**.

The **polarization P** of the medium is defined as:

$$\mathbf{P} = \frac{1}{V} [\mathbf{p}_1 + \mathbf{p}_2 + ... + \mathbf{p}_N]$$

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$

That is to say, P is the **total dipole moment per volume**. In the continuum theory, **P** is macroscopically averaged and so do not fluctuate at the atomic scale.

$$\vec{D} = \epsilon\vec{E}$$

Unless E is too high, the polarization increases linearly with E.

$$\vec{P} = x_e\vec{E}$$ **Electric Susceptibility**

Since the media is isotropic and homogeneous, χ is a scalar that do not vary in space. There are various sources of polarization but for now we assume that there is only one type of polarization source.

One consequence of the dielectric polarization is that it weakens the electric field by effectively generating **polarization charge or bound charge**. This is most easily understood in the

parallel capacitor charged with free surface charge density of σ_f.

$+\sigma_f$ $-\sigma_f$

$$E = \frac{S_f}{e_0}$$

$+\sigma_f$ $-\sigma_p$ $+\sigma_p$ $-\sigma_f$

$$E = \frac{(S_f - S_p)}{e_0}$$
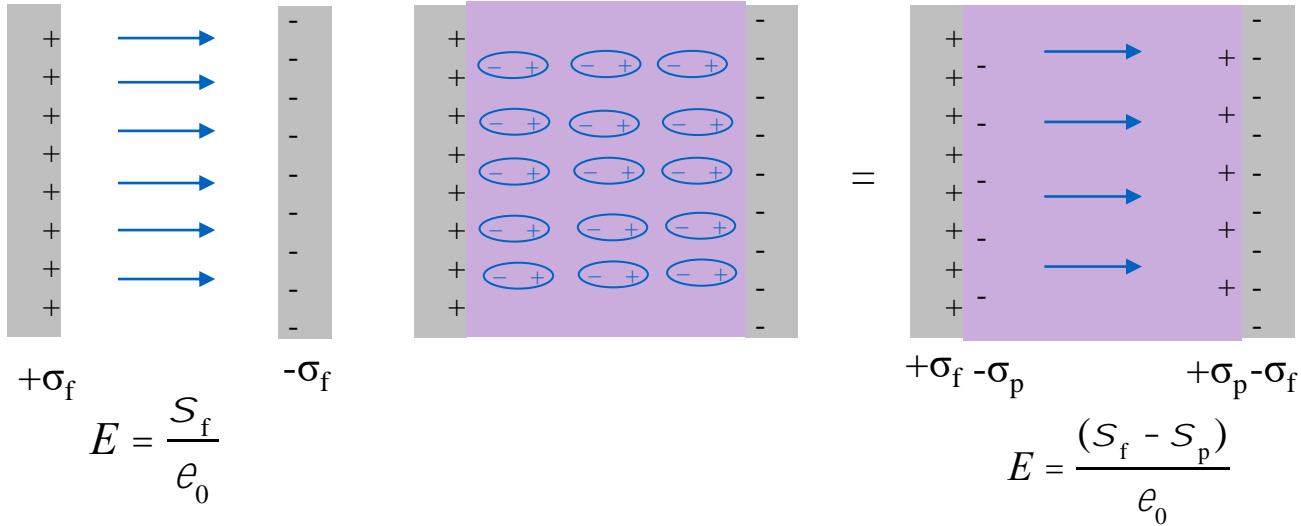
Note that we made distinction **between free and polarization charges**. They are all charges that can generate electric fields but they are treated differently within the classical electrodynamics.

$$V = E\,d$$

$$E = -\nabla\Phi$$

So what is σ_p? Take a cylinder with the surface area A and the length of L (thickness of dielectric medium). If the number density of the dipole is n,

$$nAL = N_S N_L = N_S \frac{L}{d}$$

$$N_S = nAd$$

$$S_p = q\frac{N_S}{A} = nqd = P$$

Or more simply, the total dipole moment inside the cylinder is

$$ALP = AS_pL \rightarrow P = S_p$$

8
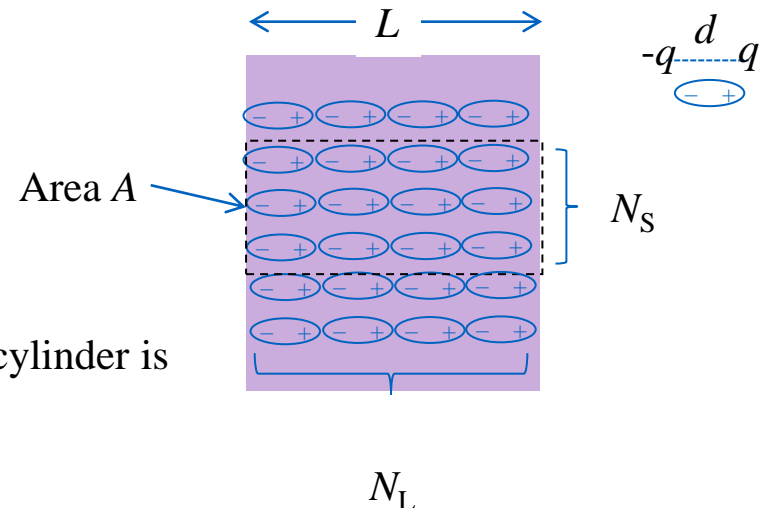
In general, the electrostatic potential by **P**(**r**) within a volume V is equivalent to that by the surface charge σ_b at the surface of V and the charge density ρ_b within V with σ_b and ρ_b given as follows:

$$\sigma_b \equiv \mathbf{P} \cdot \hat{\mathbf{n}}$$

$$\rho_b \equiv -\nabla \cdot \mathbf{P}.$$

(where $\hat{\mathbf{n}}$ is the normal unit vector),

Bound charge by divergence
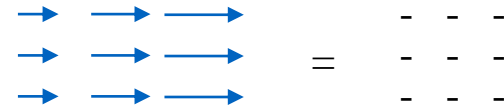
It can be easily shown that in the parallel capacitor with uniform and constant P, $\sigma_b = P$ and $\rho_b = 0$.

$$E = \frac{S_f - S_p}{e_0} = \frac{S_f - P}{e_0} = \frac{S_f - e_0 C E}{e_0}$$

$$e_0(1 + C)E = S_f$$

$$E = \frac{S_f}{e_0(1 + C)} = \frac{S_f}{e_0 e_r}$$

Relative permittivity?

The net charge appearing as a result of polarization is called bound charge $\boldsymbol{\rho_b}$

where $\varepsilon_r = 1 + \chi$ is called the **dielectric constant**. $\varepsilon_0 \varepsilon_r = \varepsilon$ is the permittivity of the material. The reduction of field intensity due to the polarization is called dielectric screening. The electric field generated by purely free charges (excluding polarization charges) is called the displacement **D**. In the parallel capacitor,

$$D = S_f = e_r e_0 E = eE = e_0(1 + C)E = e_0 E + P$$

$$\boldsymbol{D = E + 4\pi P = \varepsilon E}$$

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The Maxwell's first equation is written in matter as follows:

$$\nabla \cdot \mathbf{E} = \frac{r}{e_0} = \frac{r_f + r_b}{e_0}$$

$$\nabla \cdot \mathbf{D} = \nabla \cdot \left(e_0 \mathbf{E} + \mathbf{P} \right) = r_f + r_b - r_b = r_f$$

$$\nabla \cdot \vec{D} = 4\pi\rho_f$$

Maxwell's first equation in media. This applies not only to homogeneous and isotropic media but also to any material.

In homogeneous and isotropic media, ε_r is a constant throughout the material.

$$\nabla \cdot \mathbf{D} = \nabla \cdot (e_r e_0 \mathbf{E}) = e_r e_0 \nabla \cdot \mathbf{E} = r_f \rightarrow \quad \nabla \cdot \mathbf{E} = \frac{r_f}{e_0 e_r}$$

Should be **free charge**

Maxwell's Second Equation: Gauss's Law for Magnetism

The magnetic field is generated by currents or magnets. Unlike electric fields, there is **no point source or monopole in magnetism** such as isolated *N* or *S* poles, and opposing poles always exist in pairs. All lines of forces are closed and divergence of magnetic field always zero.

$$\nabla \cdot \vec{B} = 0$$
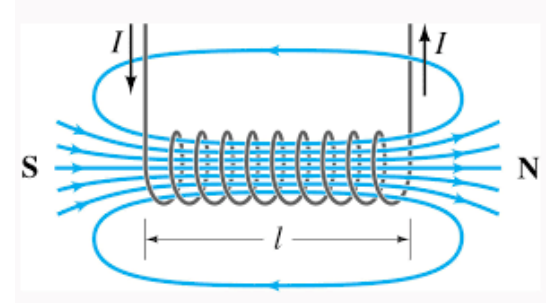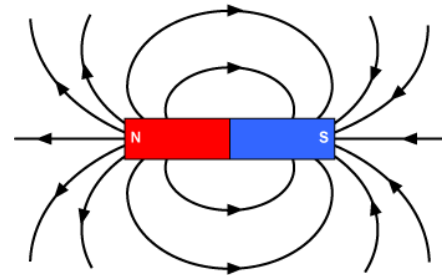
Maxwell's third equation: Faraday's law of induction (Maxwell-Faraday equation)

The Maxwell's third equation describes the fact that a potential difference (electromotive force) $\mathscr{E}$ is caused in a wire by a changing magnetic flux, which is called the Faraday's law of induction. Magnetic flux Φ is defined as

$$\Phi = \oint_S \mathbf{B} \times d\mathbf{s}$$

Therefore, the Faraday's law is mathematically written as

$$\mathscr{E} = -\frac{d\Phi}{dt}$$

Since the electromotive force is the line integration of $\mathbf{E}$ along the loop,

$$\mathscr{E} = \oint_C \mathbf{E} \cdot d\mathbf{l} = -\frac{d\Phi}{dt} = -\int_S \frac{\partial \mathbf{B}}{\partial t} \cdot d\mathbf{s}$$

From Stokes' theorem, $\quad \oint_C \mathbf{E} \cdot d\mathbf{l} = \int_S \nabla \times \mathbf{E} \cdot d\mathbf{s}$

$$\therefore \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

Move magnet right, and more lines pass through the loop.

dS

$\vec{B}$

$d\mathbf{l}$

12
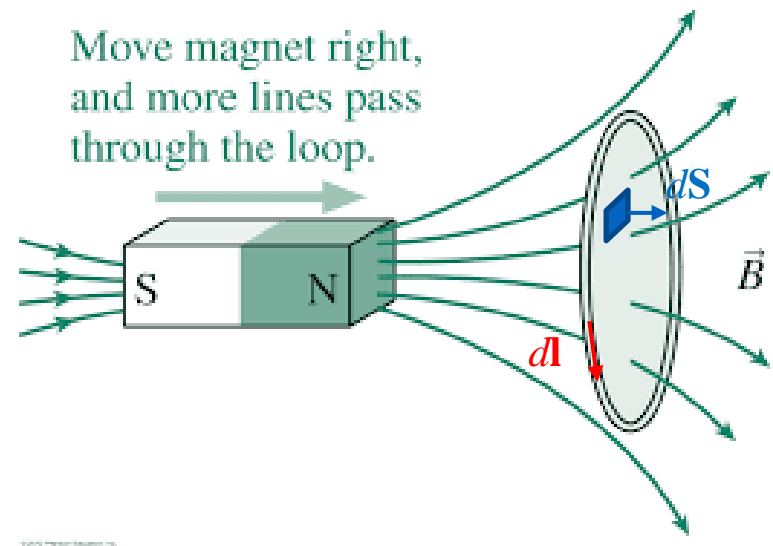
Maxwell's fourth equation: Ampere's circuital law with Maxwell's addition

The fourth Maxwell's equation concerns how the magnetic field is generated.

$$\nabla \times \mathbf{B} = m_0 \left(\mathbf{J} + e_0 \frac{\partial \mathbf{E}}{\partial t} \right)$$

Or by applying Stokes' theorem,

$$\oint_C \mathbf{B} \cdot d\mathbf{l} = \int_S \nabla \times \mathbf{B} \cdot d\mathbf{s} = \mu_0 \int_S \left(\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \cdot d\mathbf{s}$$

The first term on the right-hand side is the Ampere's circuital law. In some cases, Ampere's law leads to a paradoxical result. For instance, in the right example for a capacitor, consider the line integral of B along the path P, which results in a certain value. For the surface integral on S_1, the current flows through it so the the first term gives the consistent value, confirming the Ampere's law. However, for the surface integral on S_2, no real current flows into any area of S_2, so the surface integral is zero, which is not correct. To make things fully consistent, Maxwell proposed that the time derivative of the electric fields play like currents (the second term on the right). This is called the displacement current. In the capacitor example, as the current flows, the charges are accumulated on the plate and electric field increases between the plates, which produces the displacement current in the same direction of I.
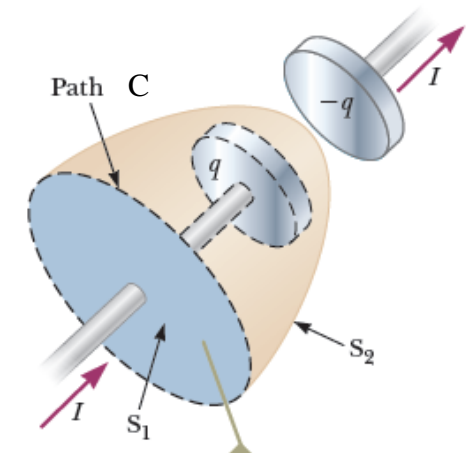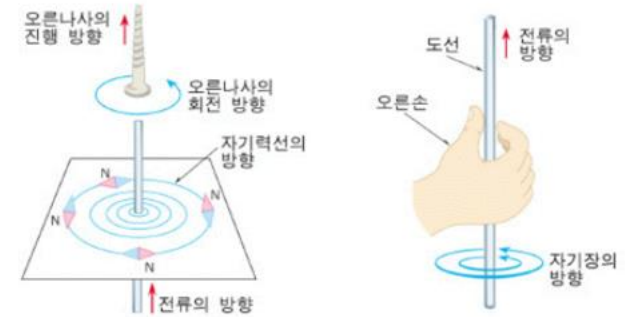
The conduction current I in the wire passes only through S_1, which leads to a contradiction in Ampère's law that is resolved only if one postulates a displacement current through S_2.

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Let's consider how this form changes in magnetic continuous media. For magnetic materials, B fields effectively induces tiny magnets located at each atomic site whose origin will be discussed in the following chapter for magnetic property.

Let's consider a simple solenoid surrounding a magnetic substance.
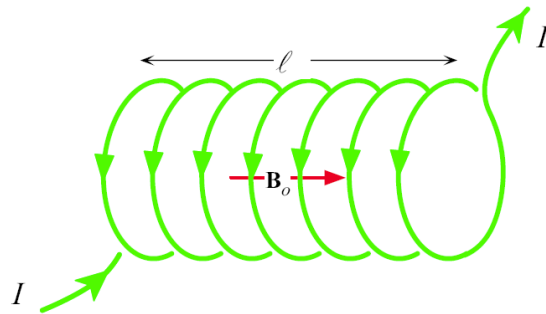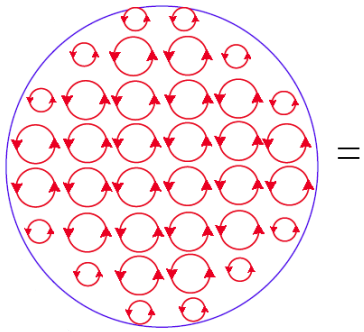

(a)
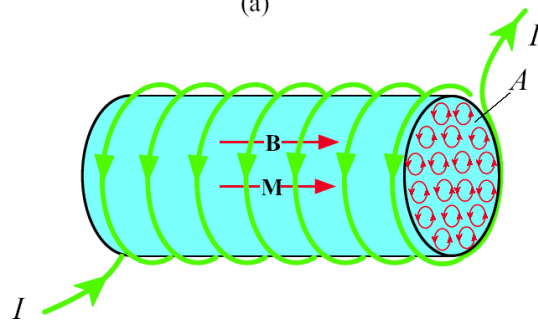
(b)

When n is the number of coils per unit length with current I flowing through them, a uniform magnetic field of B_0 is generated inside the solenoid with the magnitude of $B_0 = \mu_0 nI$. (nI is the current per unit length.) A material medium inserted into the solenoid develops atomic magnets or equivalently current loops that distribute uniformly throughout the medium. If the magnetic moment of each loop is μ_{mi}, a magnetization **M** is defined as the total magnetic moment per unit volume. If there are N atoms in the small volume ΔV.

$$\mathbf{M} = \frac{1}{\Delta V} \sum_{i=1}^{N} \mathbf{\mu}_{mi}$$

$$\mathbf{\mu} = SI\hat{n}$$
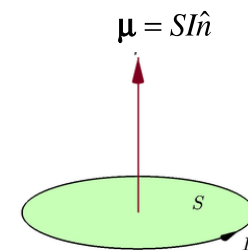
Magnetic moment and the corresponding current loop.

14

=

(In fact, all the circles should be the same.)

The cross-sectional figure indicates that elementary current loops result in surface currents. There is no internal current as adjacent currents on neighboring loops are in opposite directions.
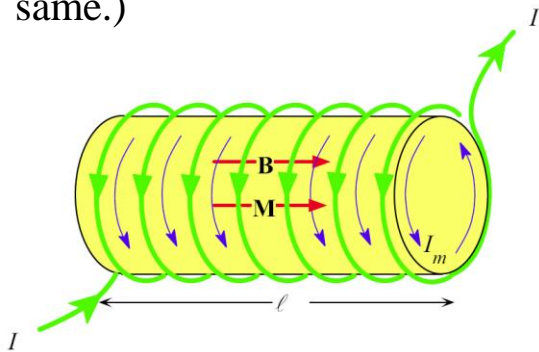
I_m: magnetization current on the surface per unit length.

Total magnetic moment = (Total current)×(Cross-sectional area) = $I_m \, \ell \, A$

Total magnetic moment = M(volume) = $M\ell \, A$

Equating the two total magnetic moments, we find

The field B in the material inside the solenoid is due to the conduction current I through the wires ($B_0 = \mu_0 nI$) and the magnetization current I_m on the surface of the magnetized medium ($\mu_0 I_m = \mu_0 M$), or $B = B_0 + \mu_0 M$

$$\mathbf{B} = \mathbf{B}_0 + m_0 \mathbf{M}$$

Magnetizing field or magnetic field intensity H: field due to external free current

$$\mathbf{H} = \frac{1}{m_0}\mathbf{B}_0 = \frac{1}{m_0}\mathbf{B} - \mathbf{M}$$

$$\mathbf{B} = m_0\left(\mathbf{H} + \mathbf{M}\right)$$

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Magnetic permeability: $\quad m = \dfrac{B}{H} = m_0 \dfrac{B}{B_0} = m_0 m_r \qquad m_r = \dfrac{B}{B_o}$ (Relative permeability)

Magnetic susceptibility χ_m: $\qquad$ (For historical reason, M is related to H rather than B.)

$$\mathbf{B} = m\mathbf{H} = m_0 m_r \mathbf{H}$$

$$\mathbf{B} = m_0(\mathbf{H} + \mathbf{M}) = m_0\left(1 + C_m\right)\mathbf{H}$$

$$\rightarrow m_r = 1 + C_m$$

So, how the fourth equation changes within the media?

$$\nabla \times \mathbf{B} = m_0\left(\mathbf{J} + e_0 \frac{\partial \mathbf{E}}{\partial t}\right) \qquad \longrightarrow \qquad \nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t}$$

Displacement current

In order to derive this, we need to consider current density contributed by the time-dependent polarization and also curl of magnetization. Please refer to Griffth pp 341 for the full derivation.

Maxwell's Equations

Inside the media in general

$$\nabla \cdot \vec{D} = 4\pi\rho_f$$

$$\nabla \cdot \vec{B} = 0$$

$$\nabla \times \vec{H} = \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

$$\vec{D} = \epsilon\vec{E} \quad \text{dielectric constant}$$

$$\vec{P} = x_e\vec{E} \quad \text{electric susceptibility}$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

$$\vec{B} = \mu\vec{H} \quad \text{magnetic permeability}$$

$$\vec{M} = x_m\vec{H} \quad \text{magnetic susceptibility}$$

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$

$$\vec{H} = \vec{B} - 4\pi\vec{M}$$

ε and μ are tensors that depend on the real space.

$$\nabla \cdot \vec{E} = 4\pi\rho$$

As it turns out, **H** is a more useful quantity than **D**. In the laboratory, you will frequently hear people talking about **H** (more often even than **B**), but you will never hear anyone speak of **D** (only **E**). The reason is this: To build an electromagnet you run a certain (free) current through a coil. The current is the thing you read on the dial, and this determines **H** (or at any rate, the line integral of **H**); **B** depends on the specific materials you used and even, if iron is present, on the history of your magnet. On the other hand, if you want to set up an *electric* field, you do *not* plaster a known free charge on the plates of a parallel plate capacitor; rather, you connect them to a battery of known *voltage*. It's the *potential difference* you read on your dial, and that determines **E** (or rather, the line integral of **E**); **D** depends on the details of the dielectric you're using. If it were easy to measure charge, and hard to measure potential, then you'd find experimentalists talking about **D** instead of **E**. So the relative familiarity of **H**, as contrasted with **D**, derives from purely practical considerations; theoretically, they're on an equal footing.

Many authors call **H**, not **B**, the "magnetic field." Then they have to invent a new word for **B**: the "flux density," or magnetic "induction" (an absurd choice, since that term already has at least two other meanings in electrodynamics). Anyway, **B** is indisputably the fundamental quantity, so I shall continue to call it the "magnetic field," as everyone does in the spoken language. **H** has no sensible name: just call it "**H**."[7]

Wave Equations for Light in Matter

We consider a homogeneous and isotropic medium without free charges. In most materials, interior free charges are rare (**in metals they exist only at the surface**).

utilize the relationship: $\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}$

$\nabla \cdot \mathbf{E} = \dfrac{r_f}{e_r e_0} = 0$

$\nabla \cdot \mathbf{H} = 0$

$\nabla \times \mathbf{E} = -m_0 m_r \dfrac{\partial \mathbf{H}}{\partial t}$

$\nabla \times \mathbf{H} = S\mathbf{E} + e_r e_0 \dfrac{\partial \mathbf{E}}{\partial t}$

$\longrightarrow$

$\nabla \times \mathbf{E} = -m_r m_0 \dfrac{\partial \mathbf{H}}{\partial t}, \quad \nabla \cdot \mathbf{E} = 0$

$\nabla \times \left(-m_r m_0 \dfrac{\partial \mathbf{H}}{\partial t} \right) = -\nabla^2 \mathbf{E}$

$-m_r m_0 \dfrac{\partial}{\partial t}(\nabla \times \mathbf{H}) = -\nabla^2 \mathbf{E}$

Substitute $\nabla \times \mathbf{H} = e_r e_0 \dfrac{\partial \mathbf{E}}{\partial t} + S\mathbf{E}$

$-e_r e_0 m_r m_0 \dfrac{\partial^2 \mathbf{E}}{\partial t^2} - m_r m_0 S \dfrac{\partial \mathbf{E}}{\partial t} = -\nabla^2 \mathbf{E}$

$$\boxed{\begin{aligned} \nabla^2 \mathbf{E} &= e_r e_0 m_r m_0 \dfrac{\partial^2 \mathbf{E}}{\partial t^2} + m_r m_0 S \dfrac{\partial \mathbf{E}}{\partial t} \\[2mm] \nabla^2 \mathbf{H} &= e_r e_0 m_r m_0 \dfrac{\partial^2 \mathbf{H}}{\partial t^2} + m_r m_0 S \dfrac{\partial \mathbf{H}}{\partial t} \end{aligned}}$$

4A.2. Light Propagation in Non-Dissipative Dielectric Media
(No Imaginary Dielectric Constant)

In insulators, the conductivity is zero ($\sigma = 0$). $\longrightarrow$ $\nabla^2 \mathbf{E} = e_r e_0 m_r m_0 \dfrac{\partial^2 \mathbf{E}}{\partial t^2}$, $\nabla^2 \mathbf{H} = e_r e_0 m_r m_0 \dfrac{\partial^2 \mathbf{H}}{\partial t^2}$

We look for the plane-wave solution: $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - Wt)}$, $\mathbf{H} = \mathbf{H}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - Wt)}$

Using

$$\nabla \cdot \mathbf{E} = i\mathbf{k} \cdot \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - Wt)} = i\mathbf{k} \cdot \mathbf{E}$$

$$\nabla^2 \mathbf{E} = -\left(\mathbf{k} \cdot \mathbf{k}\right)\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - Wt)} = -k^2 \mathbf{E}$$

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} = -W^2 \mathbf{E}$$

$$\vec{D} = \epsilon \vec{E}$$

$$\vec{B} = \mu \vec{H}$$

One can show that $\dfrac{W}{k} = v_p = \dfrac{1}{\sqrt{e_r e_0 m_r m_0}} = \dfrac{c}{\sqrt{e_r m_r}}$ where $c = \dfrac{1}{\sqrt{e_0 m_0}}$: light velocity in vacuum (3 ´ 10^8 m/s)

For medium, **ε and μ are functions of ω** or k, and the phase and group velocities are the same.

$$v_p = v_g = \frac{c}{\sqrt{e_r m_r}} = v$$

slope = $v_p = v_g$

Homogeneour media

Refractive index $\quad n = \dfrac{c}{v} = \sqrt{e_r m_r} \quad$ or $\quad v = \dfrac{c}{n}$
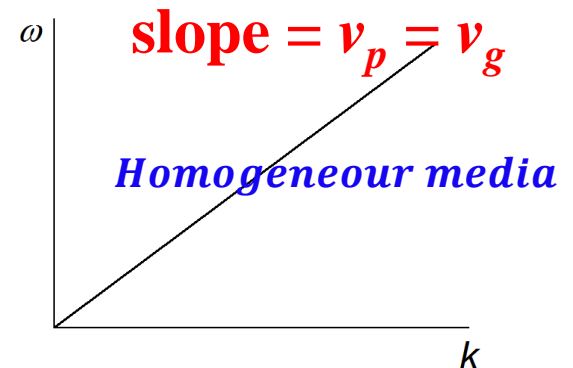
For most materials, χ_m is much smaller than 1, so $\mu_r = 1 + \chi_m \sim 1$. Therefore, the refractive index is determined by the dielectric constant.

$$n = \sqrt{e_r}$$

Additional information can be obtained by inserting plane-wave solution into Maxwell's equation

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-Wt)}, \quad \mathbf{H} = \mathbf{H}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-Wt)}$$

$$\nabla\cdot\mathbf{E} = 0 \rightarrow i\mathbf{k}\cdot\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-Wt)} = 0 \rightarrow \mathbf{k}\cdot\mathbf{E}_0 = 0 \rightarrow \mathbf{k} \wedge \mathbf{E}_0$$

$$\nabla\cdot\mathbf{H} = 0 \rightarrow \mathbf{k} \wedge \mathbf{H}_0$$

$$\nabla\times\mathbf{E} = -m_0 m_r \frac{\partial\mathbf{H}}{\partial t} \rightarrow i\mathbf{k}\times\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-Wt)} = im_0 m_r W\mathbf{H}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-Wt)} \rightarrow \mathbf{E}_0 \wedge \mathbf{H}_0 \ \& \ kE_0 = m_0 m_r WH_0$$

$$\nabla\times\mathbf{H} = e_r e_0 \frac{\partial\mathbf{E}}{\partial t} \rightarrow \mathbf{E}_0 \wedge \mathbf{H}_0$$

E_x

Direction of propagation ⟶ **k**

x

z

z

y

B_y

The **intensity of light I** is the energy flowing per unit area per second:

$$I = \frac{cne_0}{2}\left|\mathbf{E}\right|^2$$
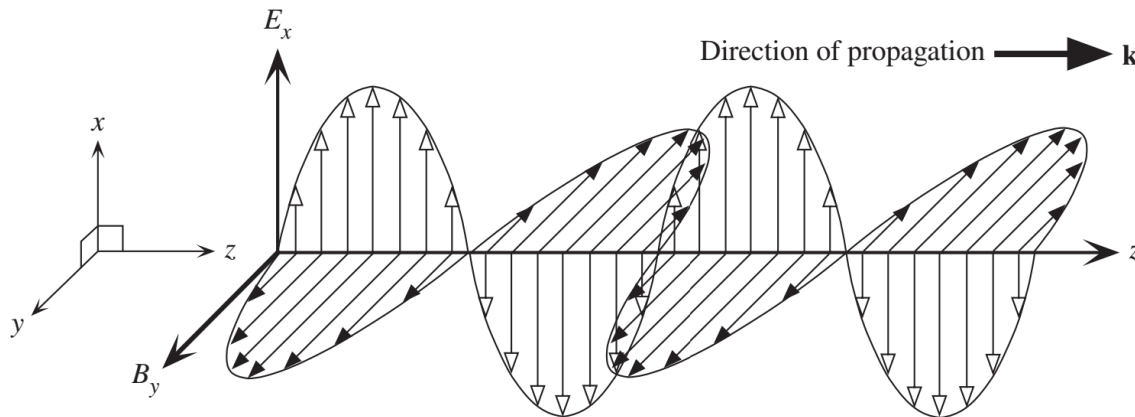
Figure 9.1 An electromagnetic wave is a traveling wave that has time-varying electric and magnetic fields that are perpendicular to each other and the direction of propagation *z*.

The results here also apply to the electromagnetic wave in vacuum ($\varepsilon_r = \mu_r = 1$)

~**Non-Dissipative** $\tilde{\varepsilon} = \varepsilon_1$

A demonstration of the Beer–Lambert law: green laser light in a solution of Rhodamine 6B. The beam radiant power becomes weaker as it passes through solution.

Dissipative Media $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$

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4A.3. Optical Absorption in Dissipative Media

As the electromagnetic wave propagates through a medium, its intensity decays because light energy is absorbed by the medium and results in mostly heat dissipation.

$$I = I_{\circ}\exp(-az)$$

(Beer's law aka Beer-Lamber law)

I : intensity

a: absorption coefficient (cm^{-1} or m^{-1})

Attenuation of Photons
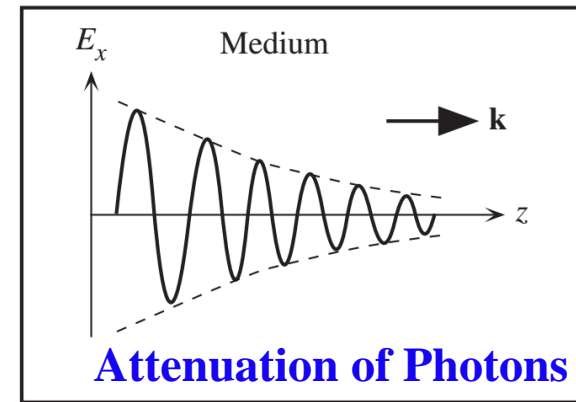
The attenuation of an electromagnetic wave in passing through a medium with absorption is usually expressed in terms of an **optical <u>absorption coefficient</u> α** as the above equation.

$1/\alpha$ is the length over which the light intensity decays by 1/e and it is called as the attenuation length or absorption length.

Implementing various microscopic mechanisms that affect polarization and conductivity into Maxwell′s equation leads to a dispersion relation that goes beyond the linear and real-valued relationship between ω and k, becoming non-linear and complex-valued. This is can be efficiently handled by generalizing the dielectric constant and hence refractive index to be **complex functions of ω**:

$$k = n\frac{\omega}{c} \rightarrow k = \tilde{n}\frac{\omega}{c} \qquad \tilde{n} = n + i\kappa$$

where κ is called **extinction coefficient,** and n is the (normal) refractive index.

Let's assume that the light propagates along z direction

$$E = E_0 e^{i(kz-\omega t)} = E_0 e^{i\left(\tilde{n}\frac{\omega}{c}z-\omega t\right)}$$

$$= E_0 e^{i\left((n+i\kappa)\frac{\omega}{c}z-\omega t\right)} = E_0 e^{-\frac{\kappa\omega}{c}z} e^{i(\frac{n\omega}{c}z-\omega t)} = E_0 e^{-\frac{\kappa\omega}{c}z} e^{i(kz-\omega t)}$$

Vacuum E_x Medium   **k**

$I = \frac{2p}{k}$

$I_0 = \frac{2p}{k_0}$

Velocity $= c/n$

For the light intensity,

$$I = \frac{cn\epsilon_0}{2}|\mathbf{E}|^2 = \frac{cn\epsilon_0}{2} E_0^2 e^{-\frac{2\kappa w}{c}z} = I_0 e^{-az}$$

$$\therefore a = \frac{2\kappa w}{c} = 2kk_0 = \frac{4pk}{I_0}$$
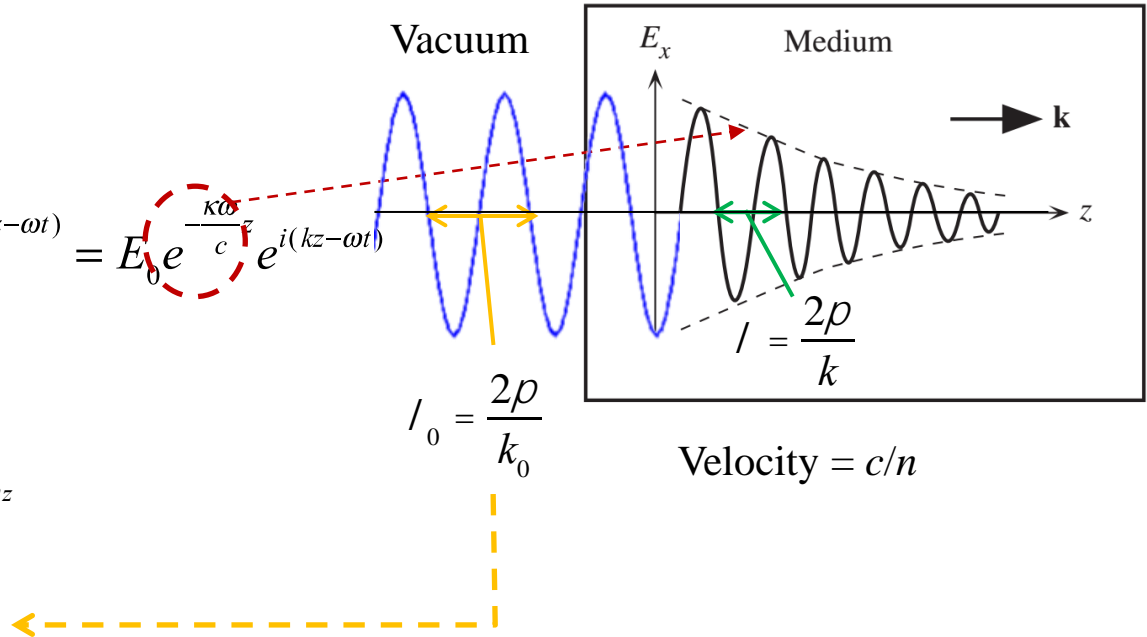
In terms of complex dielectric constant that relates to the microscopic process,

$$\tilde{n} = \sqrt{\tilde{\varepsilon}_r}$$

$$\tilde{n}^2 = \tilde{\varepsilon}_r = \varepsilon_1 + i\varepsilon_2$$

$$n^2 - \kappa^2 + 2in\kappa = \varepsilon_1 + i\varepsilon_2$$

$\longrightarrow$

$$e_1 = n^2 - k^2, \quad e_2 = 2nk$$

$$n = \frac{1}{\sqrt{2}}\left(e_1 + \sqrt{e_1^2 + e_2^2}\right)^{1/2}$$

$$k = \frac{1}{\sqrt{2}}\left(-e_1 + \sqrt{e_1^2 + e_2^2}\right)^{1/2}$$

$$\left(k = \tilde{n}\frac{\omega}{c} \right.$$

$$\left. k^2 = \tilde{\varepsilon}_r \frac{\omega^2}{c^2} \right)$$

Experimentally, n and κ are routinely measured by, for example, ellipsometry. Theoretically, ε_1 and ε_2 are directly obtained by considering microscopic mechanism.

Relations between Optical Parameters

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

Dielectric Constant

dielectric constant, $\varepsilon_{(\omega)}$

$$\varepsilon_{(\omega)} = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

refractive index, $N_{(\omega)}$

$$N_{(\omega)} = n_{(\omega)} + iK_{(\omega)}$$

$$N_{(\omega)} = \sqrt{\varepsilon_{(\omega)}}$$

$$\Rightarrow \boxed{\begin{array}{l} \varepsilon_1 = n^2 - K^2 \\ \varepsilon_2 = 2nK \end{array}}$$

$$n = \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$

$$K = \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$

Absorption Coefficient α

$\langle$Absorption coefficient, $\alpha\rangle$

$$\alpha = \frac{2\omega K}{c} = \frac{2 \cdot 2\pi\nu}{\lambda\nu} \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$

$$\therefore \alpha = \frac{4\pi}{\lambda} \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$

Refractive Index n

Extinction Coefficient κ

$$\mu_r = 1 + \chi_m \sim 1$$

Reflection at the Interface

Suppose that the light is propagating along the z-axis.

$$\mathbf{E}_i = \mathcal{C}_x^i \hat{x} e^{i(kz-wt)}$$

$$\mathbf{H}_i = H_y^i \hat{y} e^{i(kz-wt)}$$

incident

$$\mathbf{E}_r = \mathcal{C}_x^r \hat{x} e^{i(-kz-wt)}$$

reflected

$$\mathbf{H}_r = -H_y^r \hat{y} e^{i(-kz-wt)}$$

transmitted

$$\mathbf{E}_t = \mathcal{C}_x^t \hat{x} e^{i(k\tilde{z}-wt)}$$

$$\mathbf{H}_t = H_y^t \hat{y} e^{i(k\tilde{z}-wt)}$$
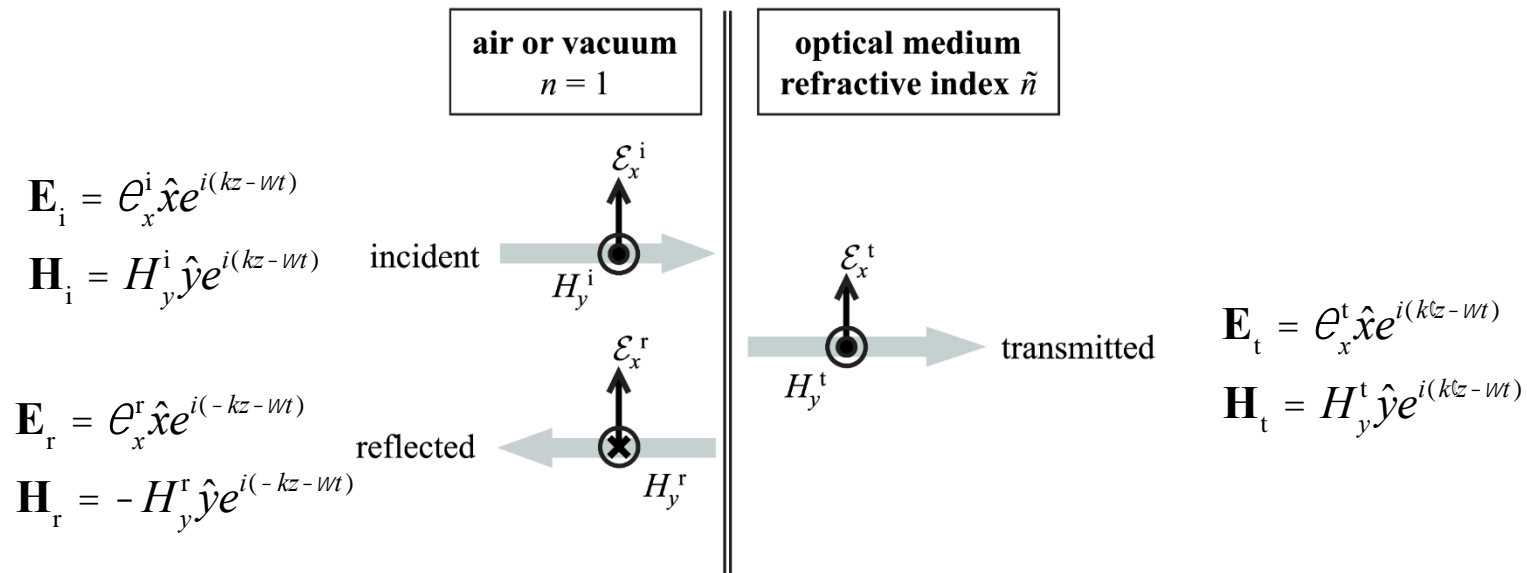
First, all the waves oscillate with the same angular frequency ω. Since the velocity of the transmitted wave is c/n, this means that the wave length is λ/n when λ is the wavelength in the vacuum.

The boundary conditions at the interface between two dielectrics tell us that the tangential components of the electric and magnetic fields are continuous at the interface ($z=0$). Since the electric field on the left side is the sum of incident and reflected beams and all electric fields and magnetic fields are parallel or antiparallel,

$$\mathcal{E}_x^i + \mathcal{E}_x^r = \mathcal{E}_x^t,$$

$$H_y^i - H_y^r = H_y^t, \quad (*)$$

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From the Maxwell's equation, we have found that $kE_0 = \mu_0\mu_r\omega H_0$,

$$H_0 = \frac{k}{\mu_0\mu_r\omega}E_0 = \frac{\tilde{n}}{c\mu_0\mu_r}E_0 \qquad \left(k = \tilde{n}\frac{\omega}{c}\right)$$

Since $\mu_r \sim 1$ for most materials, (*) becomes $\quad \mathcal{E}_x^i - \mathcal{E}_x^r = \tilde{n}\mathcal{E}_x^t$, (**)

Using (*) and (**), one can eliminate ε_x^t $\qquad \dfrac{\mathcal{E}_x^r}{\mathcal{E}_x^i} = \dfrac{1-\tilde{n}}{1+\tilde{n}} \qquad\qquad\qquad \dfrac{\mathcal{E}_x^t}{\mathcal{E}_x^i} = \dfrac{2}{1+\tilde{n}}$

The reflectivity R is the ratio of intensity between incident and reflected beams. Since the intensity is proportional to $n|E_0|^2$,

$$R = Ir/Ii, \quad T = It/Ii$$

$$R = \left|\frac{\mathcal{E}_x^r}{\mathcal{E}_x^i}\right|^2 = \left|\frac{\tilde{n}-1}{\tilde{n}+1}\right|^2 = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \qquad T\,(\text{transmittance}) = 1-R$$

For the more general case where the light is reflected at the interface between two materials with complex refractive indices of $\tilde{n}_1$ and $\tilde{n}_2$ respectively, this becomes:

$$\tilde{n}_1 \qquad\qquad \tilde{n}_2$$

$$\frac{\mathcal{E}_x^r}{\mathcal{E}_x^i} = \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2} \qquad\qquad R = \left|\frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1}\right|^2. \qquad\qquad \text{(A.55)}$$
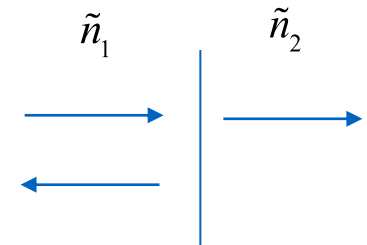
These formulas can be also used for real refractive index by simply setting $\kappa = 0$. One thing to note is that when the light reflected on a more dense media ($n_2 > n_1$), the field direction is reversed. (This is similar to fixed-end reflection (고정단반사).)

4B. Classical Model of Materials Response

4B.1. **Free Electrons within Drude Model**
4B.2. Several Sources of Polarization

We have overviewed the ingredients necessary for describing the propagation of light in the material.

The **interaction between light and matter** was considered with

conductivity and dielectric constant (polarizability) σ **and** ε. In the section, we will derive these two quantities from the microscopic picture. In doing so, we stick to the classical picture before fully considering quantum effects in the next section.

We start with the observation that since the wavelength is typically much longer than the mean free path (unless we are concerned with x-ray or γ-ray), typically longer than 100 nm, electrons feel the electric field as spatially uniform. Therefore, in discussing response of electrons or ions at r_0 under $E(r,t)$, we may assume that they are under a constant electric field of $E(r_0,t)$. Another thing to consider is that σ **and** ε **vary with frequency of the external field**. That is to say, $\sigma(\omega)$ and $\varepsilon(\omega)$.

Combining these two things, the current density at r is given by $J(r,\omega) = \sigma(\omega)E(r,\omega).$

Cu at 300 K
$v\,\tau = 35$ **nm**
$\tau = 25$ **fs**
ppt 3A-9

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4B.1. Free Electrons within Drude Model

AC Conductivity

We first consider metallic systems in which substantial numbers of free electrons exist. As the name suggests, these are systems in which the electrons experience **no restoring force** from the medium when driven **by the electric field of a light wave**. The relevant materials are metals or doped semiconductors. We first assume that there are only free electrons and no polarizable medium.

In the previous chapter, we have seen that free electrons are subject to collisions characterized by **the collision time τ** and electrons accelerate under external field between the collision. Let's recast this process in terms of the **average momentum $p(t)$** of electrons at time t (with randomly oriented $p(t)$). The average velocity is $v(t) = p(t)/m$ where m is the (effective) electron mass and the current density is $J(t) = -nep(t)/m$. When electrons are subject to a certain force $f(t)$ that depends on time but not on position, within the relaxation time approximation,

Note that $1/\tau$ corresponds to the mean probability per unit time that an electron is scattered (or mean frequency of collisions).

$$\mathbf{p}(t + dt) = \mathbf{p}(t) - \frac{dt}{t}\mathbf{p}(t) + \mathbf{f}(t)dt$$

$$\mathbf{p}(t + dt) - \mathbf{p}(t) = -\frac{dt}{t}\mathbf{p}(t) + \mathbf{f}(t)dt$$

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{t} + \mathbf{f}(t)$$

- **dt/τ is the probability to scatter during dt.**
- **$dt/\tau\ p(t)$ is the momentum lost due to the scattering.**
- **$f(t)dt$ is the impulse that is equal to the momentum change.**

We will solve this for various situations.

i) No field: $f = 0$

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{t} \to \mathbf{p}(t) = \mathbf{p}(0)e^{-t/t}$$

That is to say, the momentum decays or relaxes over the time scale of τ. Hence comes the name "relaxation" time for τ

ii) A constant (time-independent) electric field (= DC field)

$$\mathbf{f}(t) = -eE\hat{x}$$

If we look for the **steady-state solution**:

$$\frac{d\mathbf{p}(t)}{dt} = 0 \to \mathbf{p}(t) = -etE\hat{x}$$

$$\mathbf{J} = \frac{ne^2 t}{m}E\hat{x} \to S = \frac{ne^2 t}{m} : \text{DC conductivity}$$

$$\boldsymbol{J = ne v_d}$$

which we know already.

$$\boldsymbol{\sigma = ne\mu = ne^2 \tau / m^*}$$

free electron model in DC

iii) The usefulness of this equation comes with the **uniform** but **time-varying** field {or **AC** (alternating current) field}, $E(t) = E_0 \cos(-\omega t)$. This corresponds to the electric field in the **light or electric fields** in the parallel capacitor connected to the alternating currents. Mathematically, it is much more convenient to introduce the complex form.

$$\mathbf{E}(t) = \mathrm{Re}\left[\mathbf{E}_0 e^{-iWt} \right]$$

$$\mathbf{p}(t) = \mathrm{Re}\left[\mathbf{p}_0 e^{-iWt} \right]$$

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{t} - e\mathbf{E}(t)$$

$$\rightarrow -iW\mathbf{p}_0 = -\frac{\mathbf{p}_0}{t} - e\mathbf{E}_0$$

n: **carrier concentration per volume**
n: **refractive index**

$$\mathbf{p}_0 = \frac{-e\mathbf{E}_0}{1/t - iW}$$

$$\mathbf{J}_0 = -\frac{ne\mathbf{p}_0}{m} = \frac{ne^2/m\mathbf{E}_0}{1/t - iW} = S(W)\mathbf{E}_0$$

$$S(W) = \frac{ne^2/m}{1/t - iW} = \frac{ne^2 t/m}{1 - iWt} = \frac{S_0}{1 - iWt} : \text{ AC conductivity}$$

$$S_0 = \frac{ne^2 t}{m} : \text{ DC conductivity}$$

Under AC field, the conductivity becomes a complex number.

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This freedom of choice reflects a genuine ambiguity in the physical definitions of ϵ^0 and σ, which describe distinguishable physical processes only in the DC case, where σ describes the "free charges" (those that can move freely over arbitrary distances in response to the DC field) and ϵ^0 describes the "bound charges" (those that are bound to equilibrium positions and only stretched to new equilibrium positions by the DC field; see Figure K.1).
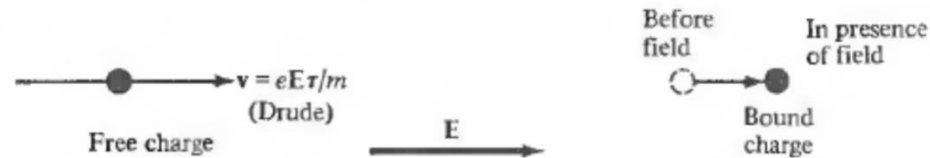
Figure K.1
The response of "free" and "bound" charges to a DC electric field. The free charge moves for as long as the field acts, but the bound charge is constrained by restoring forces, and can be displaced ("polarized") only to a new equilibrium position.

In the case of an AC field the distinction blurs. The free charges do not move arbitrarily far, but oscillate back and forth with the frequency of the field, whereas the bound charges no longer come to rest at new equilibrium positions, but also oscillate at the field frequency.

If the frequency of the field is sufficiently low ($\omega \ll 1/\tau$) the distinction can still be preserved, but on rather different grounds: The free charge velocities will respond in phase with the field (i.e., $\sigma(\omega)$ will be predominantly real) while the bound charge velocities will respond out of phase with the field (i.e., $\epsilon^0(\omega)$ will be predominantly real). At higher frequencies even this distinction disappears: The free charges can have a substantial out-of-phase response (indeed in metals, at optical frequencies, $\sigma(\omega)$ is predominantly imaginary) and the bound charges can have a considerable in-phase response (which may or may not be present at optical frequencies, depending on the material).

Plasmon = Plasma Oscillation = Nature of Charge-Density Wave

In the absence of external field, **the positive ions and electrons** distributed homogeneously and net charge is zero everywhere.

Under the external field (E_{ex}), free electrons displace by the same distance (x) that is proportional to the relaxation time. As a result, surface charges develop at the boundary of the material.

E_{ex}

$+ + + + + + + +$

E_{int}

$- - - - - - - -$ $\downarrow x$

$$w_p{}^2 = 4\pi ne^2/m^*$$
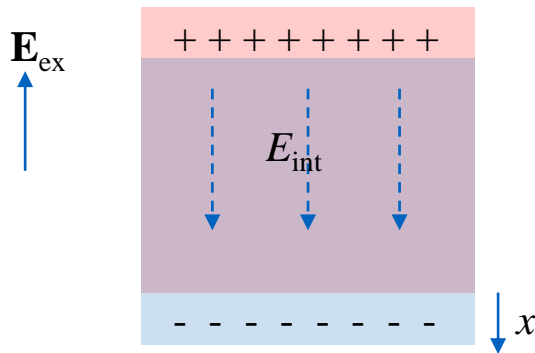
The opposite surface charges attract each other, exerting forces that try to restore the position of electrons to the equilibrium ($x = 0$). The force on the electron is

$$F = -eE_{int} = -e\frac{S}{e_0} = -e\frac{nex}{e_0} = -\frac{ne^2}{e_0}x$$

$$F = ma = m\frac{d^2x}{dt^2} = -\frac{ne^2}{e_0}x \quad \text{(harmonic oscillator)}$$

$$\frac{d^2x}{dt^2} = -\frac{ne^2}{e_0 m}x \rightarrow \text{Angular frequency} = \sqrt{\frac{ne^2}{e_0 m}} = W_p$$

In general, when electron density is not uniform, it gives rise to net charges with different polarities and electrostatic attraction among them acts as the restoring force, which results in the

resonance frequency at ω_p.

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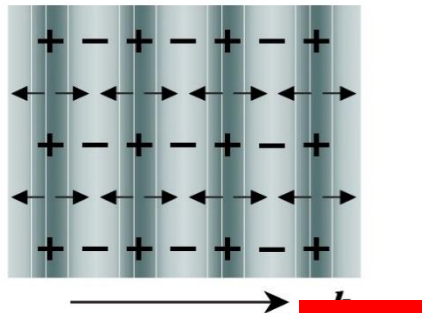
Metal (~ Free Electron Gas)

So, what is happening when $\omega < \omega_p$?

$$k = \tilde{n}\frac{\omega}{c} = i\kappa\frac{\omega}{c}$$

$$\mathbf{E} = \mathbf{E}_0 e^{i(kz - Wt)} = \mathbf{E}_0 e^{i(ik\frac{W}{c}z - Wt)} = \mathbf{E}_0 e^{-\frac{kW}{c}z} e^{-iWt}$$

Decaying or attenuating waves through medium (no propagation). **The incoming light cannot penetrate through the medium,** and is totally reflected (approximately).

$$\varepsilon(\omega) = 1 + 4\pi i\sigma(\omega)/\omega$$

from Maxwell's Eqs.
A/M Eq. (1.35)

Region of attenuation   Region of propagation

$\epsilon(\omega)$

0.5   1   1.5   2

$\frac{\omega}{\omega_p}$

$\varepsilon(\omega)$
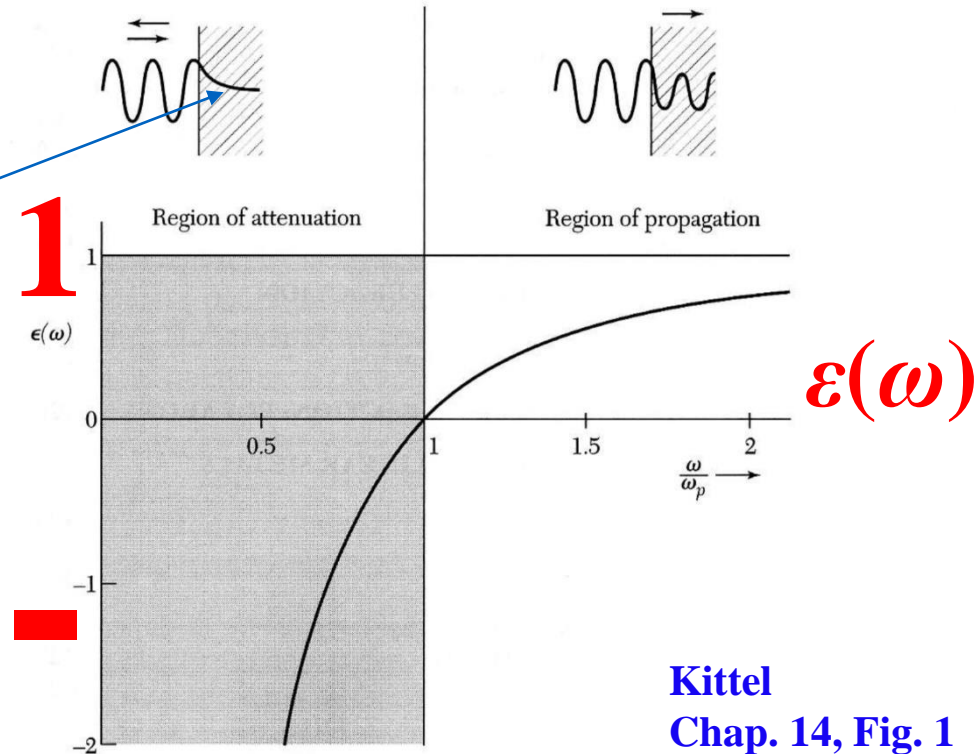
Kittel
Chap. 14, Fig. 1

Plasmon Energy (in 3D)

Table 2 Volume plasmon energies, in eV

Material	Observed	Calculated	
		$\hbar\omega_p$	$\hbar\overline{\omega}_p$
Metals			
Li	7.12	8.02	7.96
Na	5.71	5.95	5.58
K	3.72	4.29	3.86
Mg	10.6	10.9	
Al	15.3 eV	15.8	
Dielectrics			
Si	16.4–16.9	16.0	
Ge	16.0–16.4	16.0	
InSb	12.0–13.0	12.0	

$E \sim 10$ eV

$f \sim 10^{15}$ Hz

Pt = 22.9 eV
Au = 16.0 eV
Ag = 9.2 eV

Kittel
Chap. 14, Table 2

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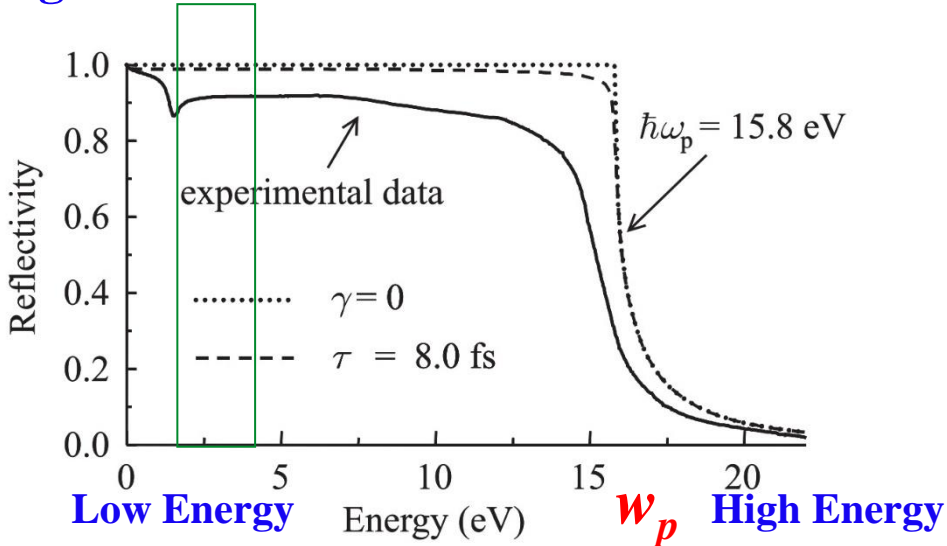
Fig. 7.2 Experimental reflectivity of aluminium as a function of photon energy. The experimental data are compared to predictions of the free electron model with $\hbar\omega_p = 15.8$ eV. The dotted curve is calculated with no damping. The dashed line is calculated with $\tau = 8.0 \times 10^{-15}$ s, which is the value deduced from DC conductivity. Experimental data from Ehrenreich et al. (1963), © American Physical Society, reprinted with permission.

Low Energy   Energy (eV) W_p High Energy

"Ultraviolet transparency of metals"
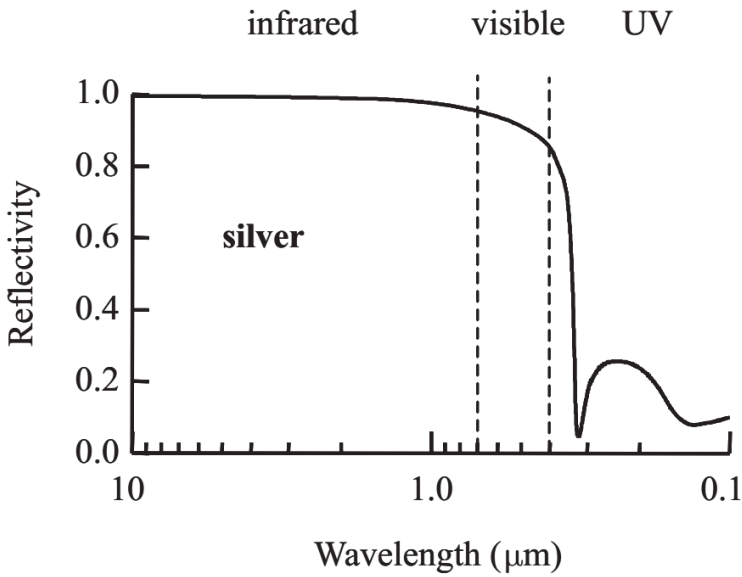
This is why metals like silver and aluminium are shiny and have been used for making mirrors for centuries.

Band theory is needed to explain why some metals (e.g. copper and gold) are coloured.

Reflections for metals

Therefore, under AC field, the conductivity becomes a complex number. How does this affect the light propagation? We plug this relation into the Maxwell equation in media.

$$\nabla^2 \mathbf{E} = e_0 m_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} + m_0 S \frac{\partial \mathbf{E}}{\partial t}$$

Using $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - Wt)}$

$$-k^2 \mathbf{E}_0 = -e_0 m_0 W^2 \mathbf{E}_0 - i m_0 S(W) W \mathbf{E}_0$$

$$k^2 = e_0 m_0 W^2 + i m_0 S(W) W = \frac{W^2}{c^2}\left(1 + \frac{iS(W)}{e_0 W}\right)$$

We have seen in the previous section that the general dispersion relation can be handled conveniently in terms of complex refractive index or dielectric constant.

$$k = \tilde{n}\frac{\omega}{c} \quad \text{or} \quad k^2 = \tilde{\varepsilon}_r \frac{\omega^2}{c^2}$$

Therefore, $\quad \tilde{\varepsilon}_r = 1 + \frac{i\sigma(\omega)}{\varepsilon_0\omega} = 1 + \frac{i}{\varepsilon_0\omega}\frac{\sigma_0}{1-i\omega\tau}$

$$= 1 - \frac{\sigma_0\tau}{\varepsilon_0}\left(\frac{1}{1+\omega^2\tau^2}\right) + i\frac{\sigma_0}{\varepsilon_0\omega}\left(\frac{1}{1+\omega^2\tau^2}\right)$$

$$= 1 - \frac{ne^2\tau^2}{\varepsilon_0 m}\left(\frac{1}{1+\omega^2\tau^2}\right) + i\frac{ne^2\tau}{\varepsilon_0 m\omega}\left(\frac{1}{1+\omega^2\tau^2}\right)$$

By defining $W_p = \sqrt{\frac{ne^2}{e_0 m}}$: plasma frequency

$$= 1 - \frac{W_p^2}{W^2}\frac{W^2 t^2}{1+W^2 t^2} + i\frac{W_p^2}{W^2}\frac{Wt}{1+W^2 t^2}$$

$$= e_1(W) + ie_2(W)$$

(Plasma is a medium with equal concentration of positive and negative charges, of which at least one charge type is mobile.)

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$$\tilde{\varepsilon}_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}\frac{\omega^2\tau^2}{1+\omega^2\tau^2} + i\frac{\omega_p^2}{\omega^2}\frac{\omega\tau}{1+\omega^2\tau^2}$$

τ in metal is typically on the order of 10 fs or 10^{-14} s and the frequency of the visible light is $> 10^{14}$ Hz, $\omega\tau = 2\pi f\tau \gg 1$ and we can neglect the imaginary part:

$$\tilde{\varepsilon}_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}
\begin{cases}
\omega < \omega_p \rightarrow \tilde{\varepsilon}_r(\omega) < 0 \rightarrow \tilde{n} = i\kappa \rightarrow R = 1 \\[2mm]
\omega > \omega_p \rightarrow \tilde{\varepsilon}_r(\omega) > 0 \rightarrow \tilde{n} = n \rightarrow R = \dfrac{(n-1)^2}{(n+1)^2} = \dfrac{(\sqrt{\tilde{\varepsilon}_r(\omega)}-1)^2}{(\sqrt{\tilde{\varepsilon}_r(\omega)}+1)^2}
\end{cases}$$

When $\tilde{n} = n + i\kappa,\ R = \dfrac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$

"Plasma reflectivity"

38
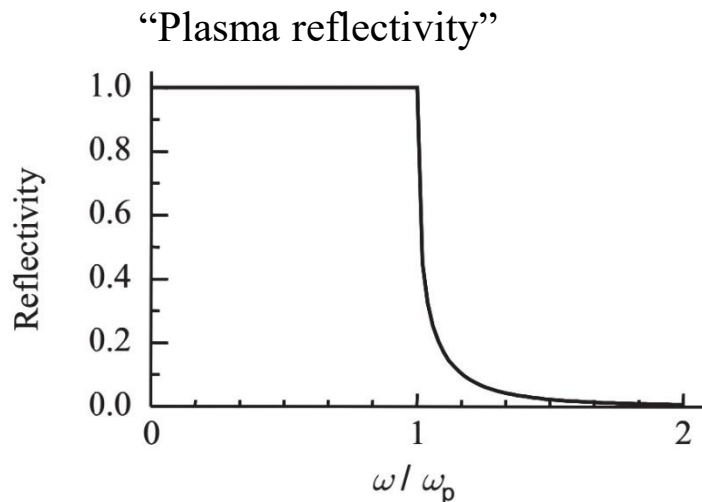
One of the best examples of plasma reflectivity effects is the reflection of radio waves from the upper atmosphere. The atoms in the ionosphere are ionized by the ultraviolet light from the Sun to produce a plasma of ions and free electrons. The plasma frequency is in the MHz range, and so the low-frequency waves used for AM radio transmissions are reflected, but not the higher-frequency waves used for FM radio or television. (See Exercise 7.2.)

39
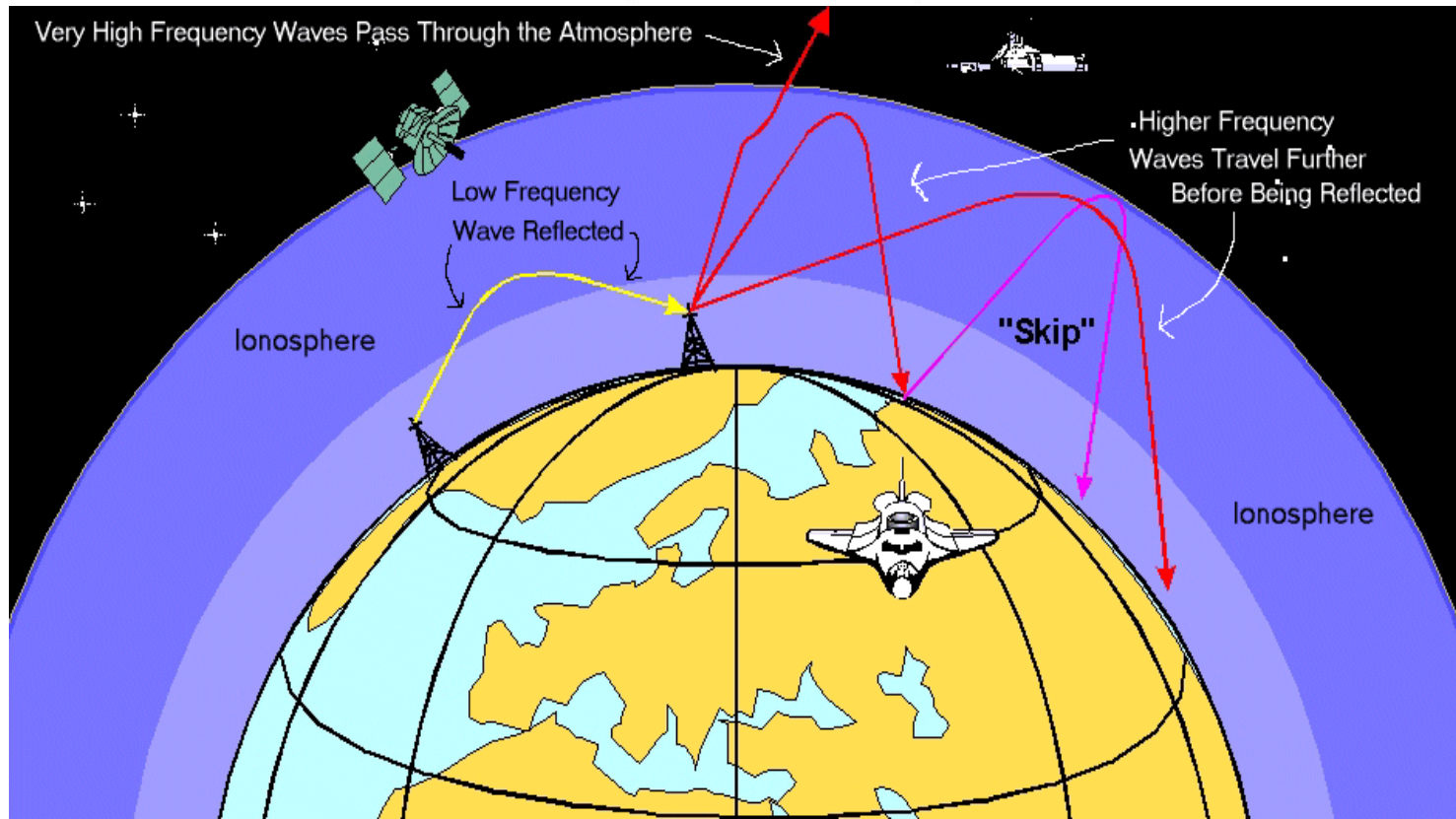
Skin Depth

At low frequencies ($\omega \ll 1/\tau$ and ω_p). In this case, $\varepsilon_2 \gg \varepsilon_1$ and

$$\left(\tilde{\varepsilon}_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}\frac{\omega^2\tau^2}{1+\omega^2\tau^2} + i\frac{\omega_p^2}{\omega^2}\frac{\omega\tau}{1+\omega^2\tau^2} \right)$$

$$\tilde{n} = \sqrt{i\varepsilon_2} = \frac{\sqrt{\varepsilon_2} + i\sqrt{\varepsilon_2}}{\sqrt{2}} \rightarrow n = \kappa = \sqrt{\frac{\varepsilon_2(\omega)}{2}} = \sqrt{\frac{\omega_p^2\tau}{2\omega}} = \sqrt{\frac{ne^2\tau}{2\varepsilon_0 m\omega}} = \sqrt{\frac{\sigma_0}{2\varepsilon_0\omega}}$$

$$\mathbf{E} = \mathbf{E}_0 e^{i(kz-Wt)} = \mathbf{E}_0 e^{i((n+ik)\frac{W}{c}z-Wt)} = \mathbf{E}_0 e^{-\frac{kW}{c}z} e^{i(\frac{nW}{c}z-Wt)}$$

The length over which the current density decays by 1/e in comparison to that at surface is called the **skin depth** (δ). Since J $\propto$ E,

$$d = \frac{c}{kW} = \frac{c}{W}\sqrt{\frac{2e_0 W}{s_0}} = \sqrt{\frac{2}{s_0 W m_0}}$$ **~5 nm in Pt at 4 eV**

4B.2. Several Sources of Polarization
i) Electronic Polarization

Now we turn our attention to the polarization in the dielectric medium.

In materials, there are **several sources of polarization**. First, we focus on the polarization by **electrons bound to nucleus**. This can be well captured by the Lorenz model with certain **resonance frequencies**. For simplicity, let's assume that one electron vibrates.

(a) A neutral atom in $E = 0$

(b) Induced dipole moment in a field
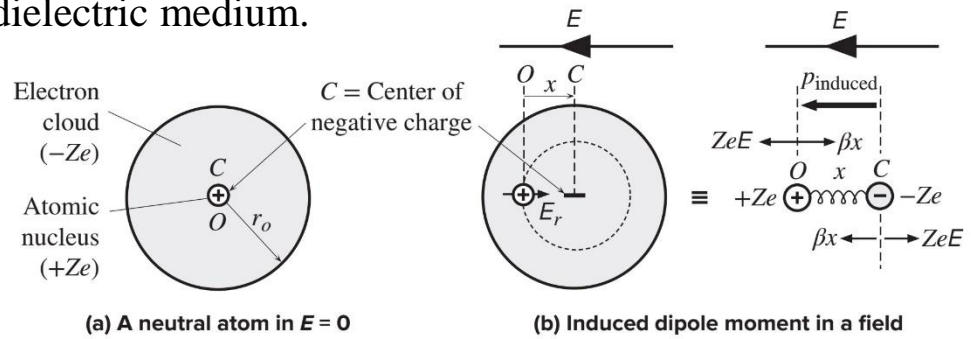
$$m\frac{d^2x}{dt^2} + mg\frac{dx}{dt} + mW_0^2 x = -eE(t)$$ ~~γ: damping rate~~

Using the complex notation, $E(t) = E_0 e^{-iWt}, \quad x(t) = x_0 e^{-iWt}$

$$-mW^2 x_0 e^{-iWt} - imgW x_0 e^{-iWt} + mW_0^2 x_0 e^{-iWt} = -eE_0 e^{-iWt}$$

$$x_0 = \frac{-eE_0/m}{W_0^2 - W^2 - igW}$$

If the number density of dipoles are N, the polarization P is given by

$$P = -Nex = \frac{Ne^2}{m}\frac{1}{W_0^2 - W^2 - igW}E_0 e^{-iWt} = \frac{Ne^2}{m}\frac{1}{W_0^2 - W^2 - igW}E(t) \xrightarrow{\text{In general}} \mathbf{P} = \frac{Ne^2}{m}\frac{1}{W_0^2 - W^2 - igW}\mathbf{E}$$

This gives the dielectric susceptibility:

$$\mathbf{P} = e_0 C\mathbf{E} \rightarrow C = \frac{Ne^2}{e_0 m}\frac{1}{W_0^2 - W^2 - igW}$$

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i) Electronic Polarization

$$e_r(W) = 1 + C = 1 + \frac{Ne^2}{e_0 m} \frac{1}{W_0^2 - W^2 - igW}$$

$$e_1(W) = 1 + \frac{Ne^2}{e_0 m} \frac{W_0^2 - W^2}{\left(W_0^2 - W^2\right)^2 + \left(gW\right)^2}, \qquad e_2(W) = \frac{Ne^2}{e_0 m} \frac{gW}{\left(W_0^2 - W^2\right)^2 + \left(gW\right)^2}$$

~eV
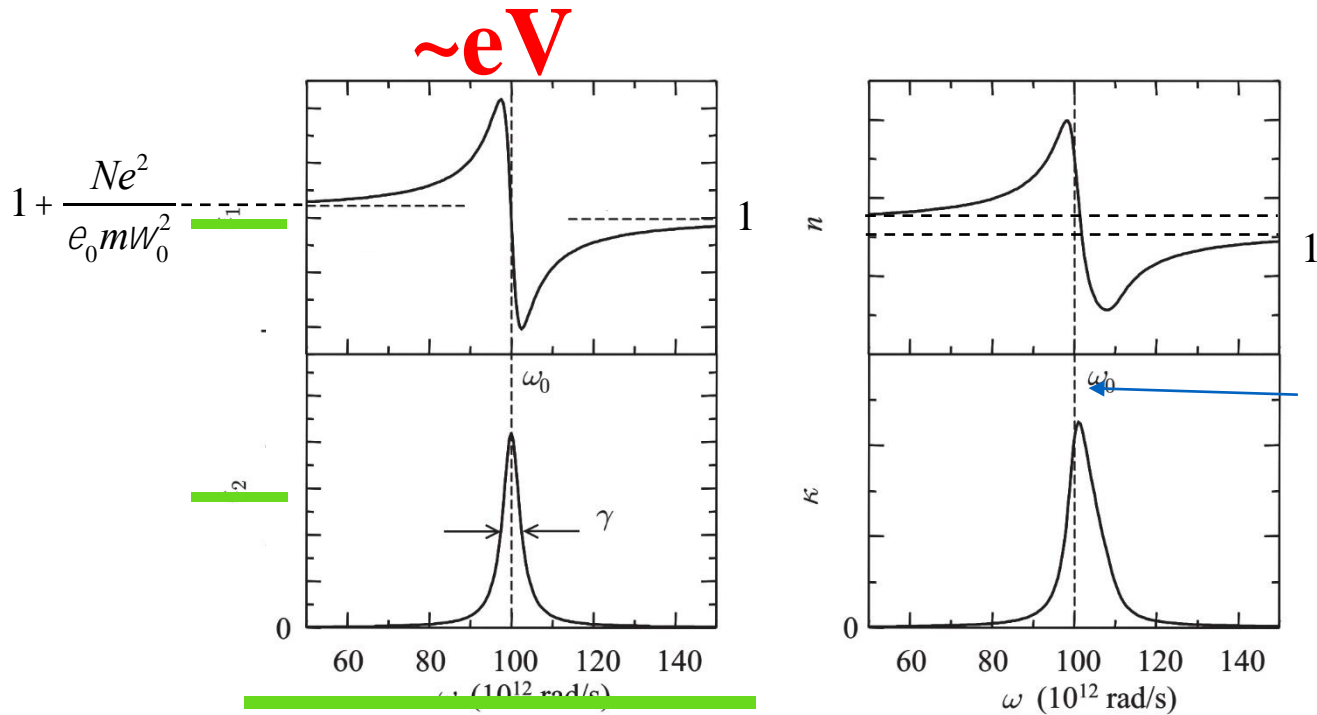
Energy is lost or absorbed by the medium most strongly at the resonant frequency. This is called the **dielectric loss**.

Fig. 2.4 Frequency dependence of the real and imaginary parts of the complex dielectric constant of a dipole oscillator at frequencies close to resonance. The graphs are calculated for an oscillator with $\omega_0 = 10^{14}$ rad/s, $\gamma = 5 \times 10^{12}$ s^{-1}, $\epsilon_{st} = 12.1,0$ and $\epsilon_\infty = 10$. Also shown is the real and imaginary part of the refractive index calculated from the dielectric constant.

The medium is polarized when ω is lower than ω_0. However, when ω becomes much higher than ω_0, the oscillator does not exhibit any dielectric polarization. This is because the oscillator cannot follow the field change. Consequently, the refractive index steps down as ω crosses ω_0.

Other Polarization Mechanisms: ii) Ionic Polarization
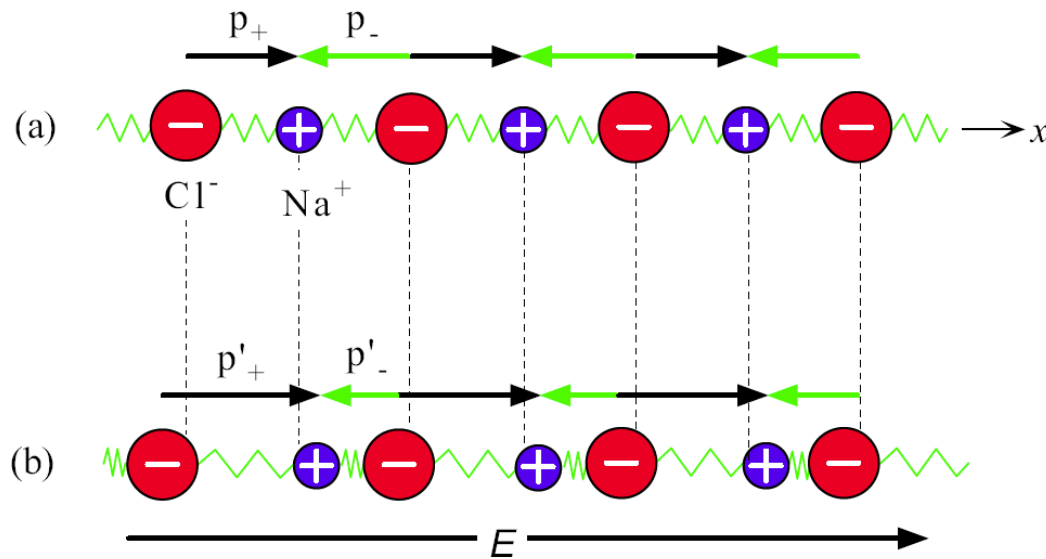
(a) A NaCl chain in the NaCl crystal without an applied field. Average or net dipole moment is zero.

(b) In the presence of an applied field the ions become slightly displaced which leads to a **net average dipole moment**.

This corresponds to the **optical mode**. Therefore, the resonance frequency in the ionic polarization corresponds to the **optical frequency (~10 THz)** that corresponds to **infrared (IR)** . Those **phonon modes** that can respond to IR are called to be IR-active. The lattice absorption by the IR-active phonon modes is specifically called the Reststrahlen (German: residual rays) absorption.

~THz

On the other hand, the polarization by the acoustic mode is possible (piezoelectric response), but its magnitude is much smaller than for the optical mode.

In materials such as water, the molecules have permanent dipole moments even before the application of external field. However, they are randomly distributed so the average dipole moment (p_{av}) is equal to zero.

Under the external field, the dipole moment tends to align parallel to the field while the magnitude remains to be same. This results in the finite p_{av}. The following figure is on the example of HCl liquid.
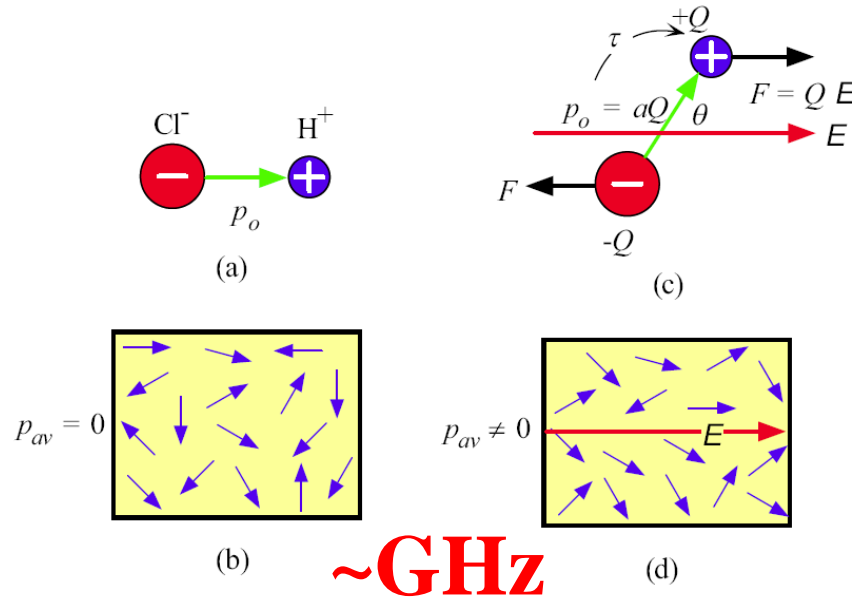
(a) A HCl molecule possesses a permanent dipole moment p_0.

(b) In the absence of a field, thermal agitation of the molecules results in zero net average dipole moment per molecule.

(c) A dipole such as HCl placed in a field experiences a torque that tries to rotate it to align p_0 with the field E.

(d) In the presence of an applied field, the dipoles try to rotate to align with the field against thermal agitation. There is now a net average dipole moment per molecule along the field.

iii) Dipolar Polarization

From the thermodynamic consideration, the average dipole moment (p_{av} or $\bar{p}$) under the constant E field at thermal equilibrium is given by

$$\bar{p} = \frac{1}{3}\frac{p_0^2 E}{kT} = a_d E$$

p_0: permanent dipole moment
α_d: polarizability

Suppose that the DC field is suddenly drops from E_0 to E at time $t = 0$. The induced dipole moment $\bar{p}$ has to decrease from $\alpha_d E_o$ to the final value of $\alpha_d E_1$ to establish the thermal equilibrium. The decrease is achieved by random collisions of molecules in the gas. The related collision time is τ_d that has the similar meaning of the collision time τ in electron scattering. τ_d is called the dipolar relaxation time and microscopically, τ_d corresponds to the time scale of molecular rotation. The excess dipole moment $\bar{p} - \alpha_d E$ will decay in a similar way to the momentum relaxation.

$$\bar{p}(t + dt) = \bar{p}(t) - \frac{dt}{t_d}\left(\bar{p}(t) - a_d E_1\right)$$

$$\frac{d\bar{p}(t)}{dt} = -\frac{\bar{p}(t) - a_d E_1}{t_d}$$

In general, for the time-varying AC field of $E(t)$

$$\frac{d\bar{p}(t)}{dt} = -\frac{\bar{p}(t) - a_d E(t)}{t_d}$$

P(t)

E(t)
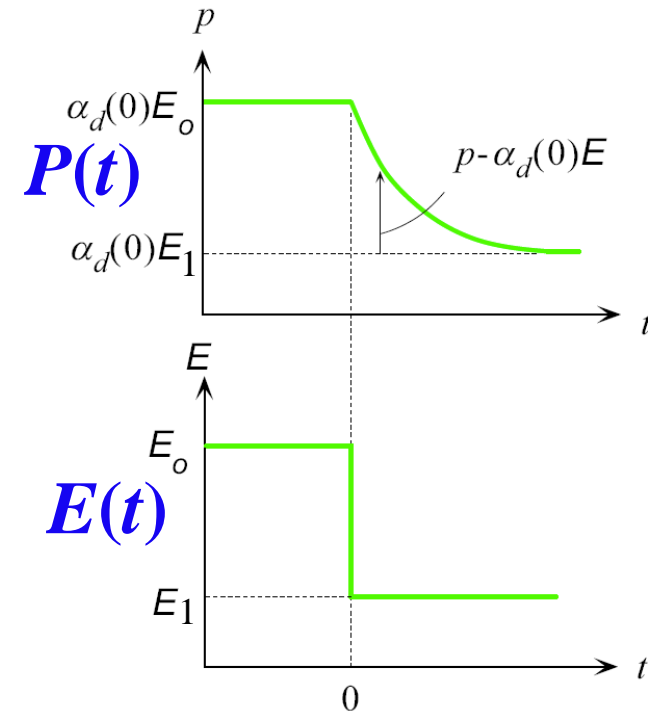
Schematic Figure Only

iii) Dipolar Polarization

The response of the dipole under AC field can be treated in complex notation as usual:

$$E(t) = E_0 e^{-iWt}, \quad \overline{p}(t) = \overline{p}_0 e^{-iWt}$$

$$\frac{d\overline{p}(t)}{dt} = -\frac{\overline{p}(t) - a_d E(t)}{t_d} \rightarrow -iW\overline{p}_0 = -\frac{\overline{p}_0 - a_d E_0}{t_d}$$

$$\overline{p}_0 = \frac{a_d E_0}{1 - iWt_d} \qquad \searrow \overline{p}(t) = \frac{a_d}{1 - iWt_d} E(t)$$

If N is the number density of dipolar molecules, $\quad P = N\overline{p}(t) = \dfrac{Na_d}{1 - iWt_d} E, \quad C = \dfrac{Na_d}{e_0} \dfrac{1}{1 - iWt_d}$

$$\tilde{\varepsilon}_r(\omega) = 1 + \chi = 1 + \frac{N\alpha_d}{\varepsilon_0} \frac{1}{1 - i\omega\tau_d}$$

$$\begin{cases} \varepsilon_1(\omega) = 1 + \dfrac{N\alpha_d}{\varepsilon_0} \dfrac{1}{1 + (\omega\tau_d)^2} \\ \\ \varepsilon_2(\omega) = \dfrac{N\alpha_d}{\varepsilon_0} \dfrac{\omega\tau_d}{1 + (\omega\tau_d)^2} \end{cases}$$

Schematic Figure Only

~GHz
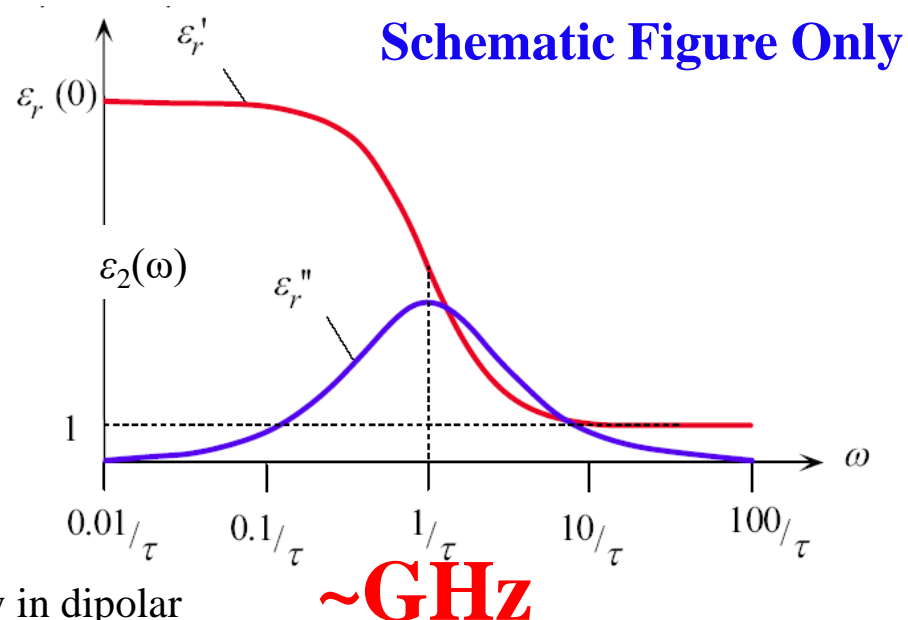
The relaxation time characterizes the resonance frequency in dipolar polarization. The difference is that $\varepsilon_1(\omega)$ decreases monotonically rather than sharp oscillation as in the Lorentz oscillator.

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iii) Dipolar Polarization

2.4 GHz for microwave oven

Schematic Figure Only

ε_1 ε_r ε'

ε_2 ε_i ε''
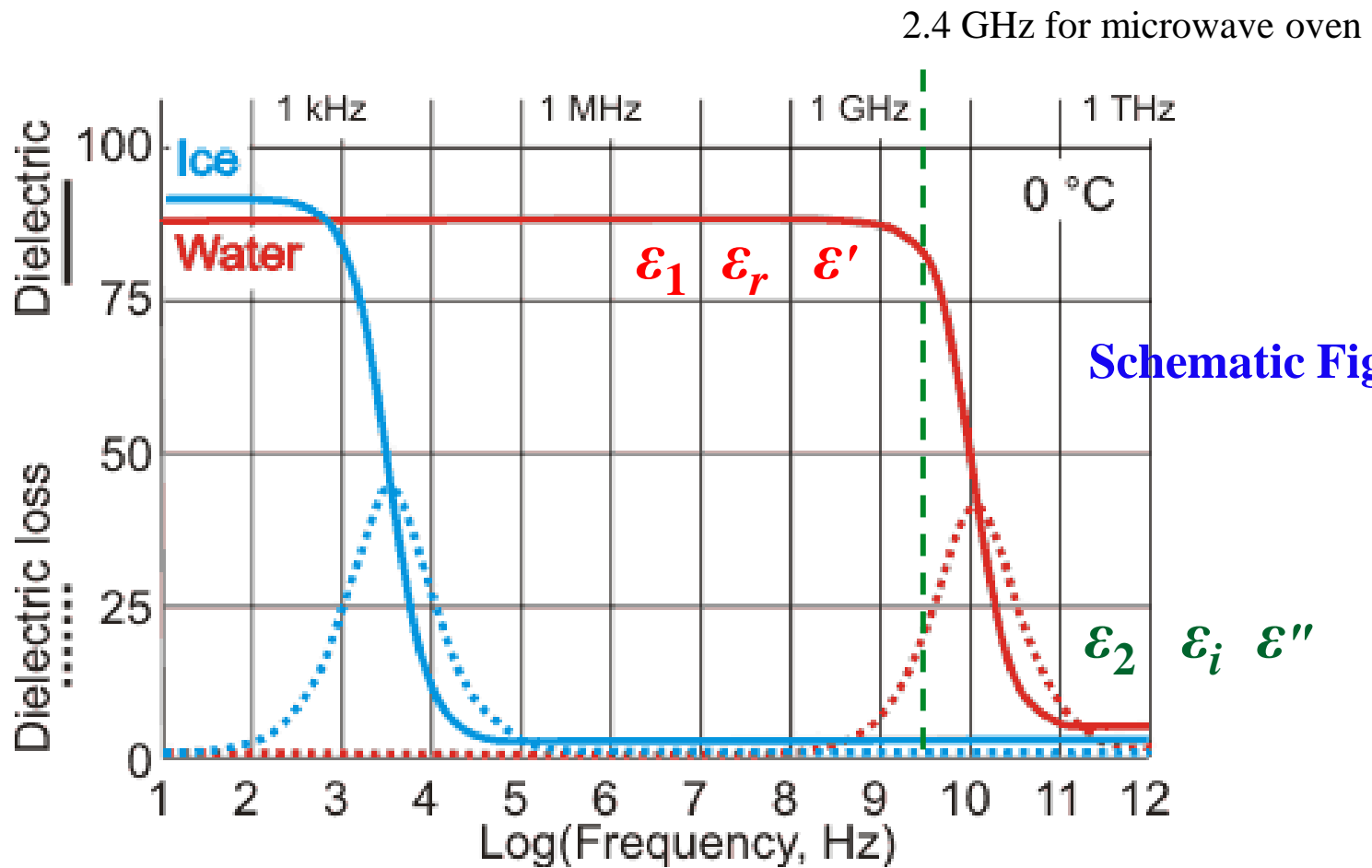
$\tau_d \sim 100$ ps (water) and $\sim$ ms (ice)

http://www1.lsbu.ac.uk/water/microwave_water.html

Other Polarization Mechanisms: iv) Interfacial Polarization

~100 μm

Schematic Figure
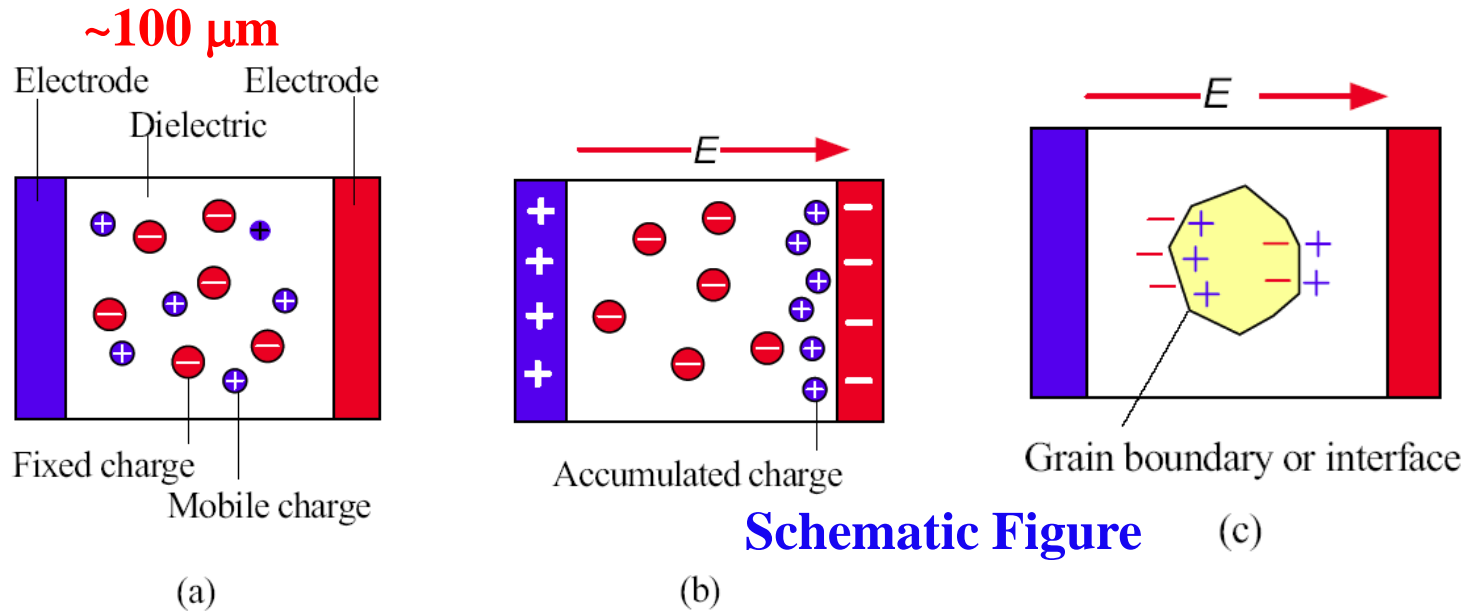
The relaxation time for the interfacial polarization is much longer than the dipolar relaxation time. Therefore, the dielectric loss occurs at much lower frequencies.

(a) A crystal with equal number of mobile positive ions (ex. H+, Li+) and fixed negative ions. In the absence of a field, there is no net separation between all the positive charges and all the negative charges.

(b) In the presence of an applied field, the mobile positive ions migrate toward the negative charges and positive charges in the dielectric. The dielectric therefore exhibits interfacial polarization.

(c) Grain boundaries and interfaces between different materials frequently give rise to Interfacial polarization.

The frequency dependence of the **real and imaginary parts of the dielectric constant** in the presence of **interfacial**, **dipolar**, **ionic**, and, **electronic** polarization mechanisms.
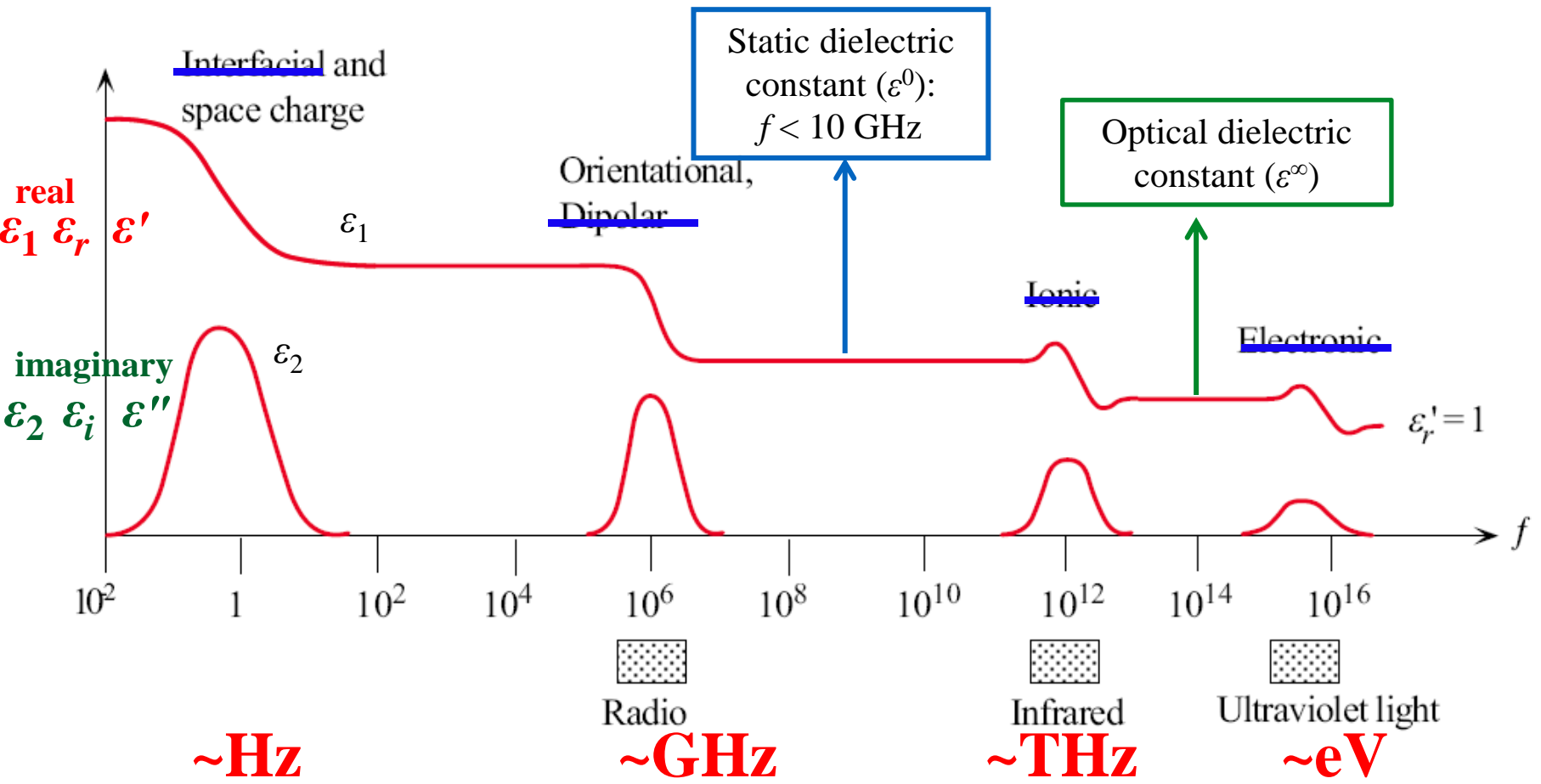
4C. Quantum Phenomena: Absorption

4C.0. Vertical Transition and Photon Absorption

4C.1. Interband Transition: Semiconductor

4C.2. Interband Transition: Metal

4C.3. Exciton

4C.4. Free Carrier Absorption

4C.5. Surface Plasmon

4C.6. Raman Spectroscopy

The classical theory of polarization and conductivity gave good account of light-matter interactions on a macroscopic scale. Nevertheless, fine details are not fully captured by this approach, which requires consideration of quantum effects.

By the quantum effects we mean the **band structure for electrons** and particle nature for waves (**photon** for electromagnetic waves and **phonon** for lattice vibrations). The light-matter interactions are essentially **among these three parties**. The quantum process explicitly describes how electrons absorb or emit photons, possibly together with absorption or emission of phonons. Therefore, it directly relates to the absorption and emission process within the material. We will first focus on the photon absorption.

4C.0. Vertical Transition and Photon Absorption

Since the photon and phonon are **bosons**, they can be created or annihilated. In Chap. 3B, we have seen that in the electron-phonon collision, the **energy and crystal-momentum conservations** should be satisfied in the collision process. The same principle applies to the interaction involving the photon: the energy and momentum should be conserved. (The crystal momentum for electrons or phonons.) For instance, suppose that an **electron in (n_i, k_i)** absorbs **one photon with (ω, k)** and occupy a **new electron state (n_f, k_f)** which should be empty before the transition (due to the Pauli exclusion principle). The related conservation laws are:

$\varepsilon(n_f, \mathbf{k}_f) - \varepsilon(n_i, \mathbf{k}_i) = \hbar\omega$: energy conservation

$\hbar\mathbf{k}_f - \hbar\mathbf{k}_i = \hbar\mathbf{k}$: (crystal) momentum conservation

$\left.\begin{array}{c}\\ \\\end{array}\right\}$ Conservation laws for photon absorption

Since the wave length of photon is longer than ~100 nm or 1000 Å, $|\mathbf{k}|$ is smaller than 10^{-3} Å^{-1}.

The Brillouin zone length is on the order of Å^{-1}, therefore,

$\mathbf{k}_f - \mathbf{k}_i \simeq 0$

This to say, **k is so small** that **k_f is essentially identical to k_i**. This corresponds to the **vertical transition** as shown in the band diagram.

This is because the light is so light (**massless**) that it can deliver meaningful momentum. The transition should be between different bands, and so it is **interband transition**. As a result, **electron-hole pair** is created. Note that the transition requires that the final state is empty because of Pauli exclusion principle.
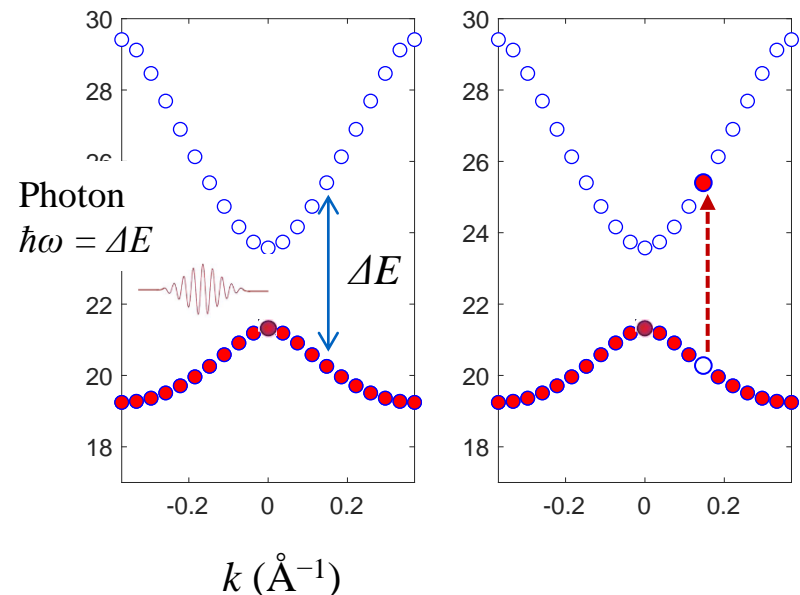
? Multi-Photon Absorption Process by One Electronic Transition ?

The absorption of photon occurs in a **probabilistic** way (that follows the Fermi golden rule). Suppose that a packet of photons are passing through the medium. After they pass over a certain length, say 1 μm, **some percentage of photons are absorbed** and lost from the packet. For the next travel over the same length, the same percentage of the remaining photons will be absorbed. In this way, the intensity of light that is equal to the number photons, is reduced exponentially, which is nothing but the Beer's law.

The **absorption coefficient** is typically in the range of 10^3 - 10^5 cm^{-1} for semiconductors. That is to say, for a photon to be absorbed, it should travel at least **100 nm**, going past over hundreds of lattice sites and electrons. This means that the absorption probability is rather low.

Thicknesses of
LED
Solar Cells
Water Splitting

This also implies that **multi-photon absorption process** in which **several photons are simultaneously absorbed by one electronic transition happens in a much lower chance** than single-photon absorption.

In the next sections, we will examine electronic transitions in various situations.

4C.1. Interband Transition: Semiconductor

$$D(E) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

Free Electron Model
(spin-up or spin-down)

Direct Bandgap

The insulators have an energy gap between occupied and unoccupied states. This means that the photon is not absorbed by electrons with its energy below the energy gap.

For the direct-bandgap material such as GaAs and InAs, the absorption starts right from the bandgap if photon energy $\hbar\omega$ is equal to E_g. The absorption creates one electron in the conduction band bottom and one hole in the valence band top.

With higher photon energies, more electron-hole pairs are available for the absorption because DOS increases with the square-root of electron or hole energies. This increases the **absorption coefficient** as **more transitions can happen**.

$$\alpha \propto (\hbar\omega - E_g)^{1/2}$$
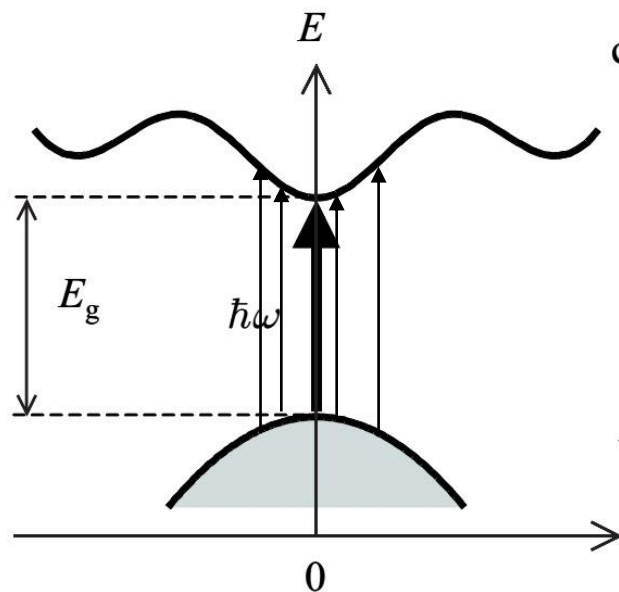
(a) Direct band gap
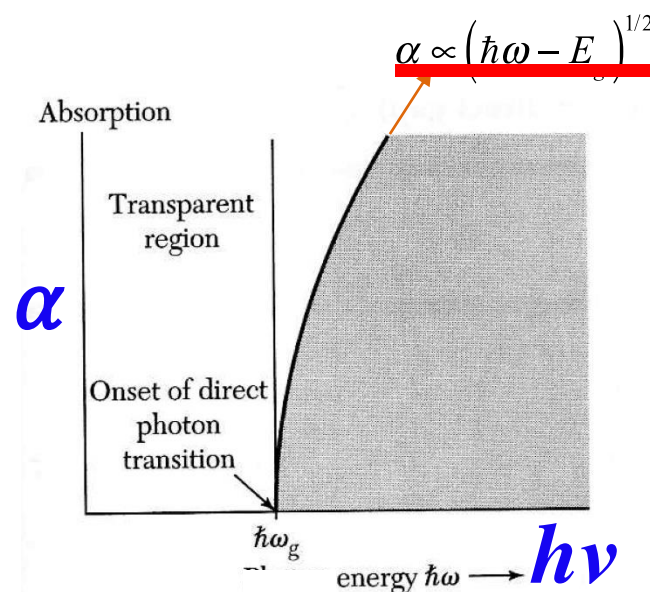
JDOS: why depends only on square root? If the transition can happen over any two states then JDOS should be the square of square-root. However, for the vertical transition, only one state is available for the transition for the given valence state. Therefore, JDOS still follows square root.
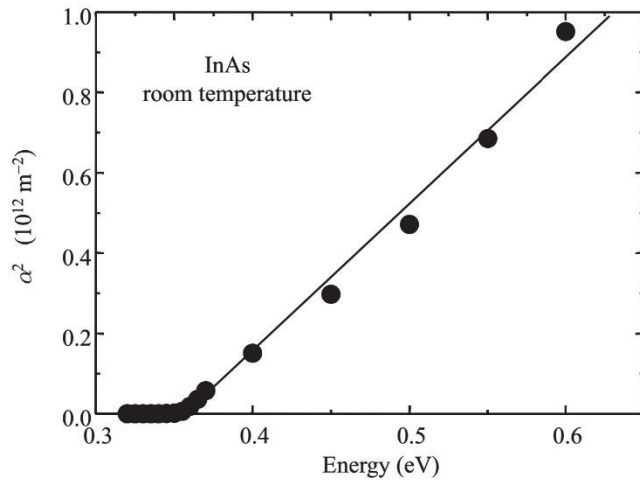
Fig. 3.6 Square of the optical absorption coefficient α versus photon energy for the direct gap III–V semiconductor InAs at room temperature. The band gap can be deduced to be $0.35\,\mathrm{eV}$ by extrapolating the absorption to zero. Data from Palik (1985).

GaAs

Absorption Edge

$E_g(T)$

α

E_g $h\nu$

54
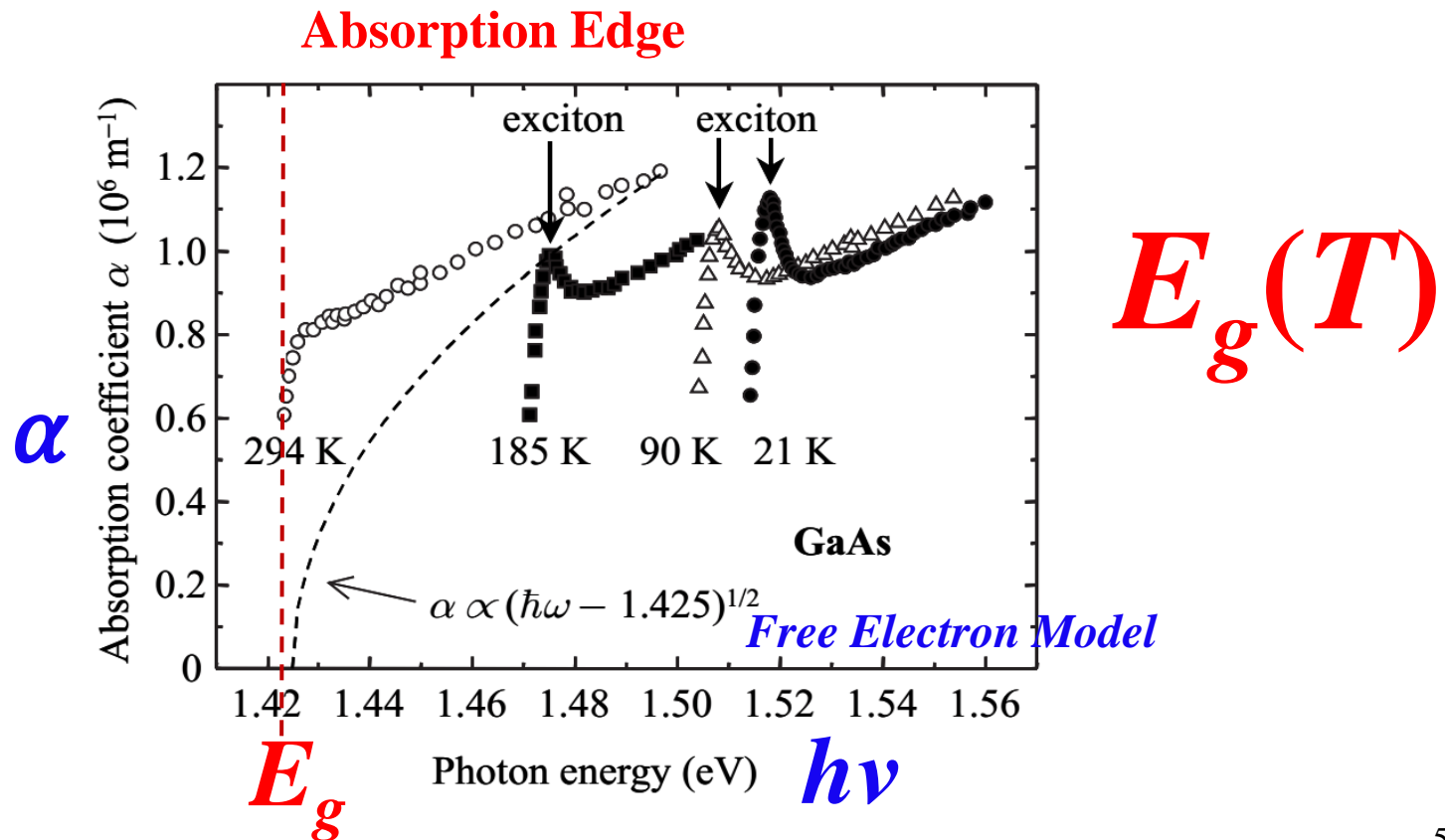
Indirect Bandgap

For the indirect-bandgap material such as Si, the absorption at the bandgap cannot be accomplished solely by one photon because the momentum is not conserved. However, the absorption is allowed if one additional phonon absorbed or emitted to conserve the momentum. The energy of phonon is typically small (**~THz)**, so it does not affect much the energy conservation between photon and electron. The **simultaneous involvement of photon and phonon** corresponds to the second-order process, and **the transition rate** is much lower than for the vertical (direct) transition involving only one photon. At higher energies, the vertical transition starts to occur and absorption coefficient increases rapidly as in the direct-bandgap material.
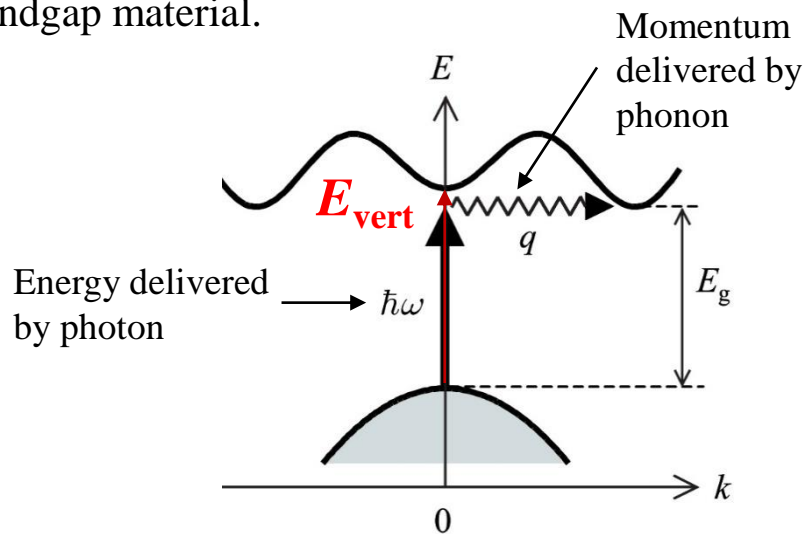
In detail, phonon can be **annihilated** or **created**.
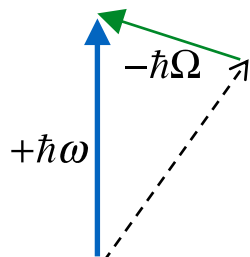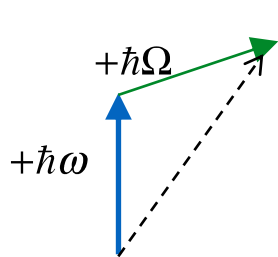
Phonon **Annihilation** (Photon + Phonon = Electron Transition)

Phonon **Creation** (Photon = Phonon + Electron Transition)
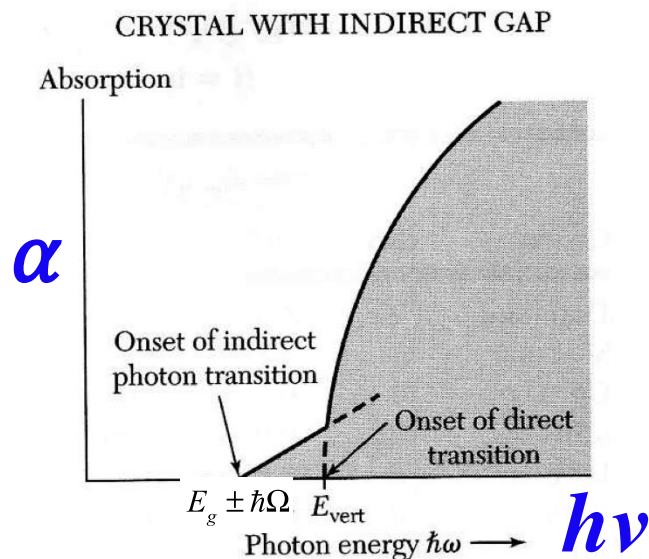
It can be shown that

$$\alpha^{\text{indirect}}(\hbar\omega) \propto (\hbar\omega - E_{\text{g}} \mp \hbar\Omega)^2 .$$

Note that <u>dependence on energy</u> is <u>different from the direct absorption.</u>

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- The absorption is much more efficient in direct-bandgap material.
- This is why solar cells with high efficiency employs direct-gap material such as GaAs.
- But, GaAs is much more expensive than Si.
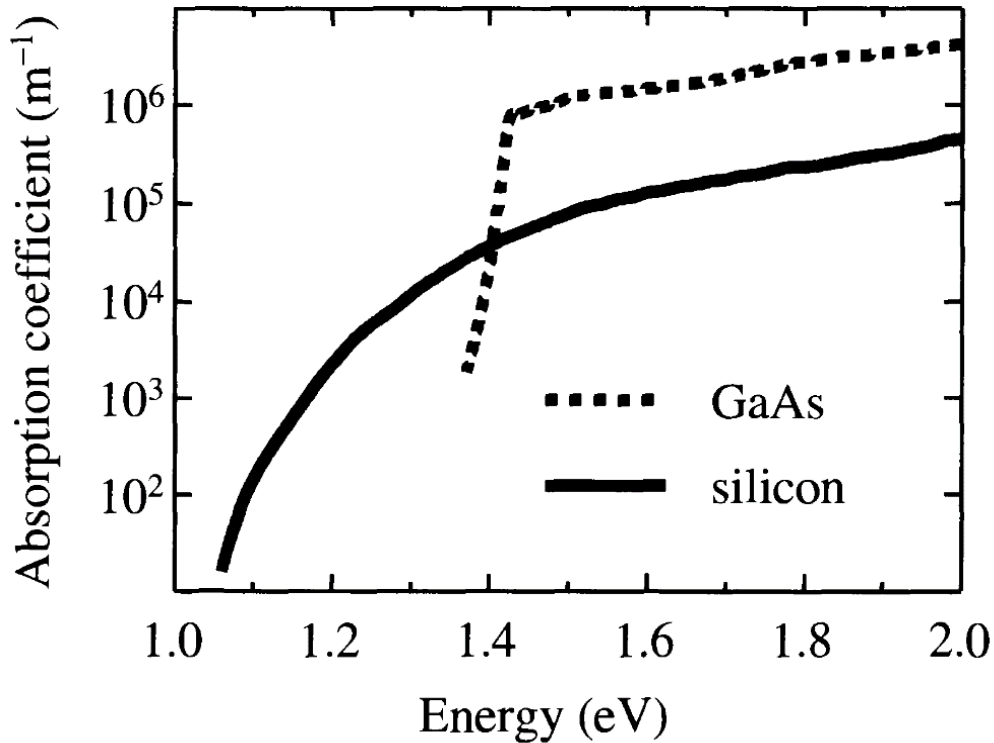
Fig. 3.8 Comparison of the absorption coefficient of GaAs and silicon near their band edges. GaAs has a direct band gap at 1.42 eV, while silicon has an indirect gap at 1.12 eV. Note that the vertical axis is logarithmic. After [3].

Optoelectronics
Bandgap Engineering of Si for a Direct Bandgap?

Germanium: Indirect Bandgap.

E_g (300 K) E_g (20 K)

(a) 291 K, phonon absorption, phonon emission, 20 K

(b) 300 K germanium

$$\alpha \sim (\hbar\omega - E_g^{dir})^{1/2}$$

Indirect transition   Direct transition

E_g
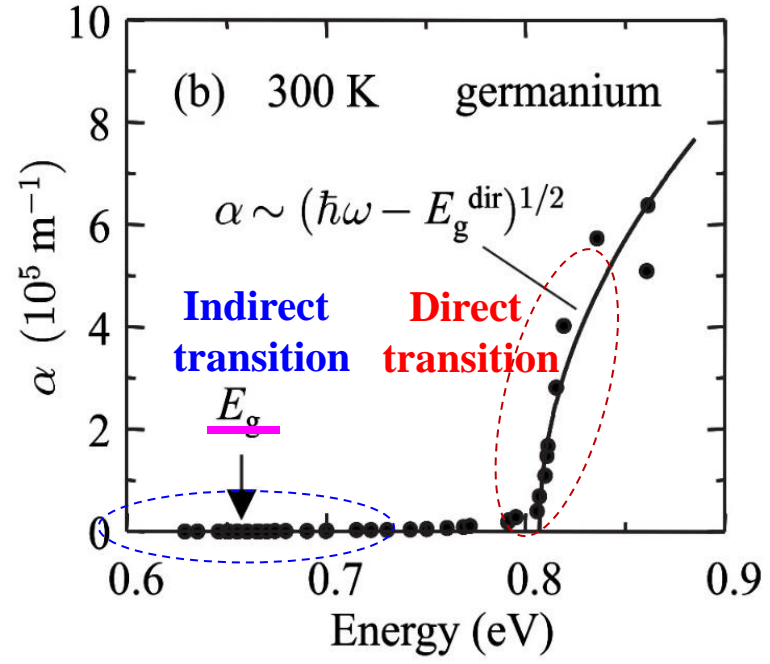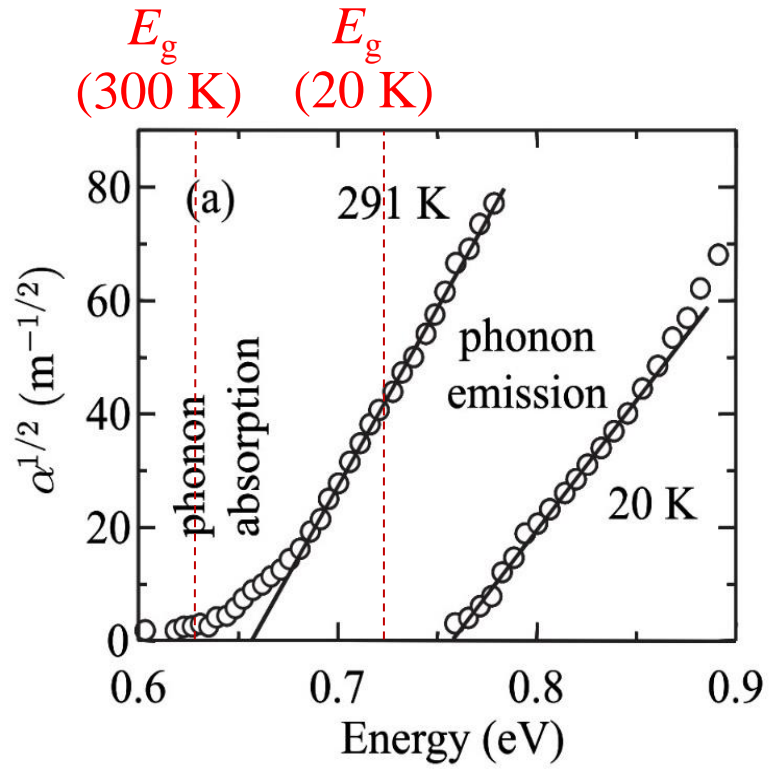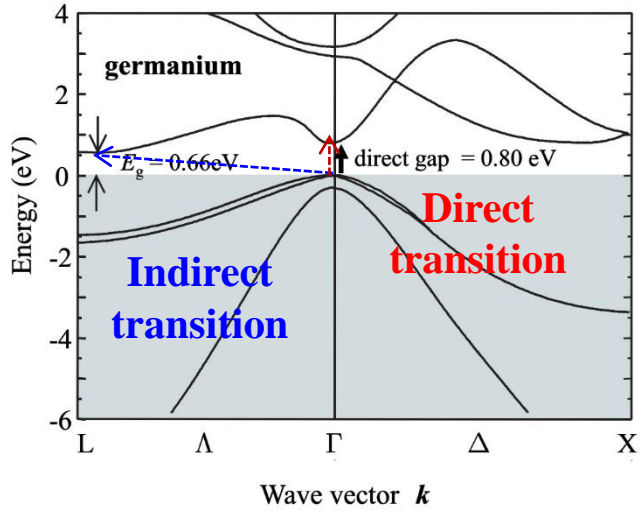
Phonon emission is possible at all temperatures, but phonon absorption is only possible if phonons are thermally excited. Therefore, at 291 K, the absorption occurs at energies even lower than E_g. In contrast, at very low temperatures at 20 K, little phonons are available such that the absorption can start by emitting phonons. At 20 K, the onset energy is 0.76 eV while the energy is known to be 0.74 eV at this temperature. The energy difference of 0.02 eV well corresponds to the phonon energy at L point.

From the band structure, we can see that **numerous electronic transitions are possible** at various energy values. This results in the **reduced reflectivity of the experimental data** compared to the **near-perfect plasma reflectivity**. Note that this electronic transition is completely independent from the plasma oscillations, and it occurs within the attenuation length from the surface.

In the dash-boxed region, the occupied and unoccupied bands are separated by **~1.5 eV** with a similar dispersion. Therefore, many electrons are available for the absorption specifically at this energy, leading to a strong absorption. This explains the **reflectivity dip at 1.5 eV**.

Aluminum
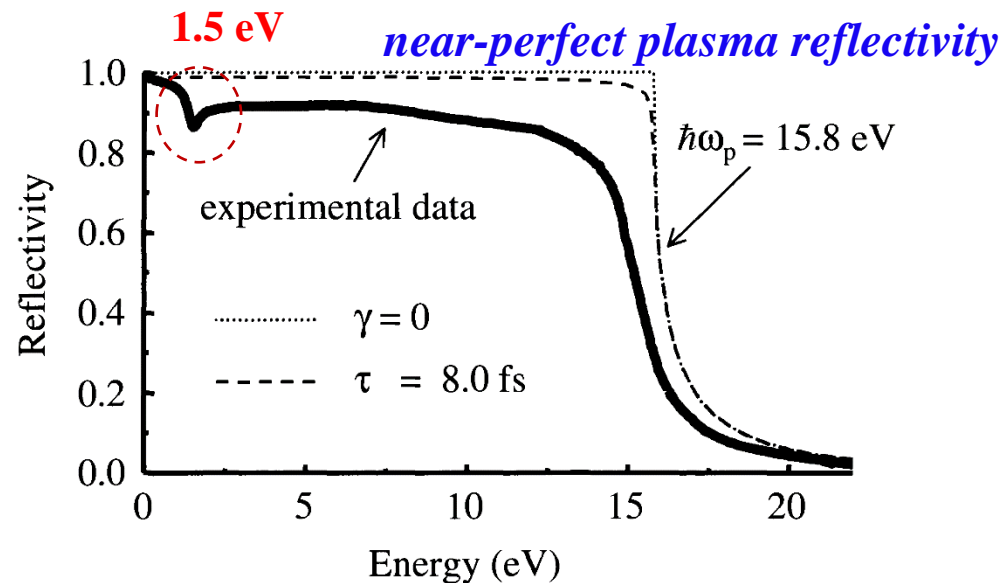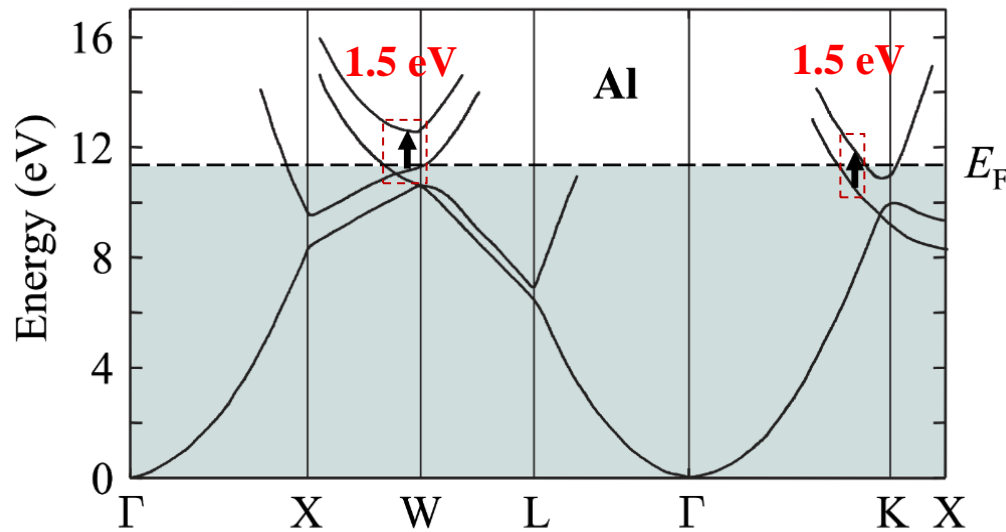
- ## Copper (Cu)

The noble metals such as Cu, Ag, and Au have the same $d^{10}s^1$ valence configuration and share similar band structures: the **fully occupied and flat *d* bands** lie a few eVs below the Fermi level while the s^1 **electron form a dispersive, free-electron *s* band**.

Unlike Al, the interband transition within the free electron band occurs at high energies above the visible light (~4 eV). Rather, the absorption starts **from the occupied *d* band to unoccupied *s* band** which has the threshold energy of ~2 eV (560 nm) in the case of Cu, and absorptions at higher energies are all available because *d* **band is flat while *s* band is dispersive**.

Because of this, the reflectivity of Cu sharply drops as the photon energy increases above ~2 eV. Therefore, photons from red to yellow are strongly reflected.

Calculated Band Structure of Cu
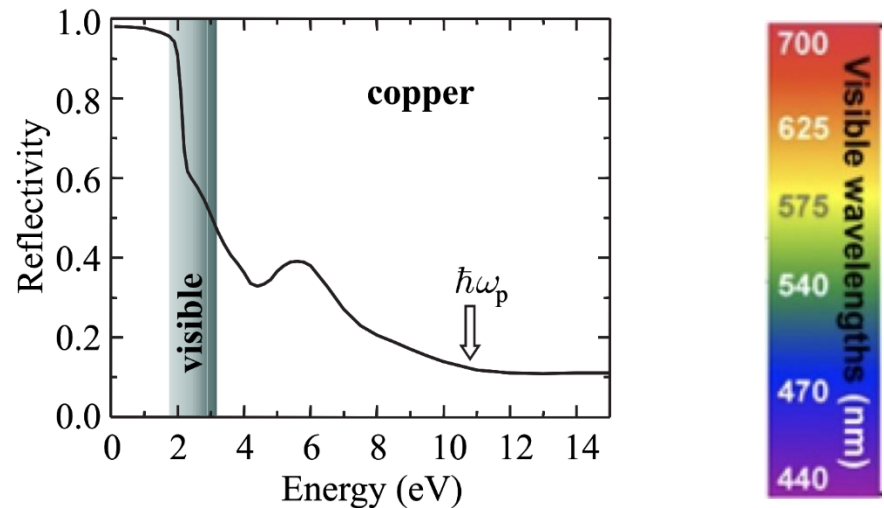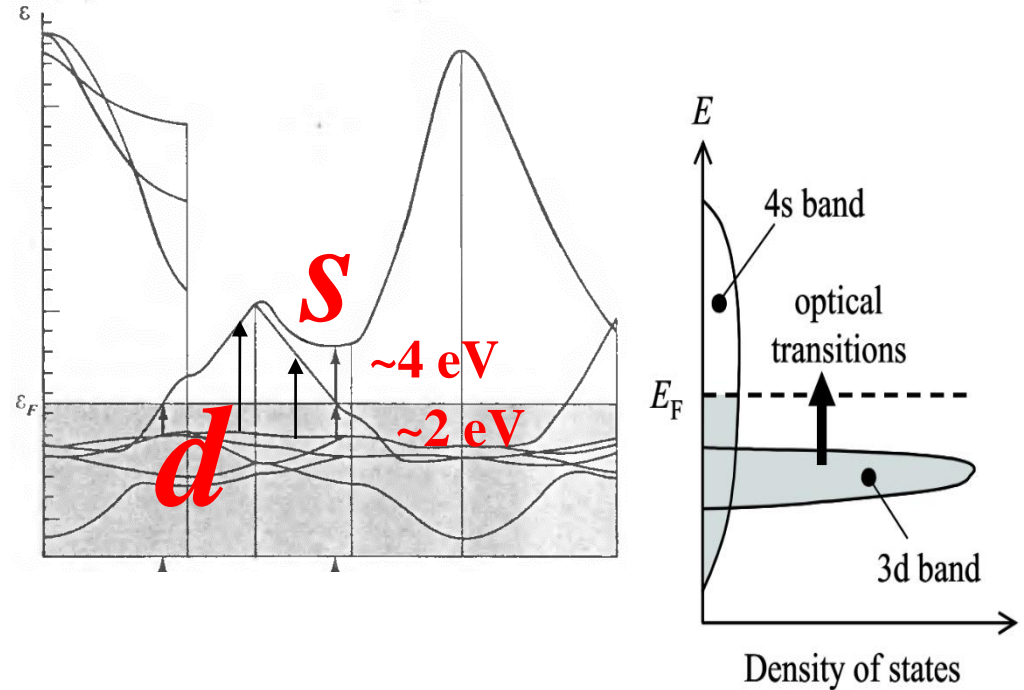
• Cu, Ag, and Au

For Ag, the absorption edge is around 4 eV, so it can reflect the whole range of visible light. This is consistent with the experimental reflectivity. The same explanation applies to Au. The characteristic reflectance can explain the color of noble metals.

Al

Cu

Ag

Au
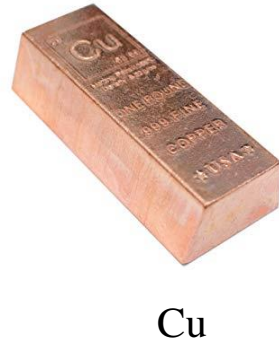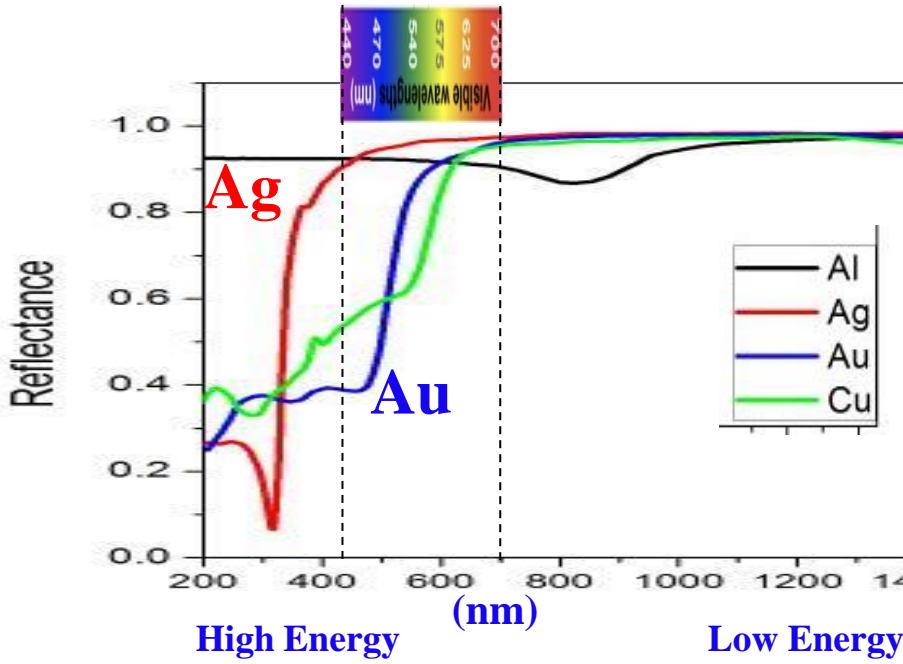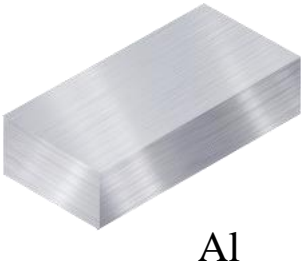
4C.3. Exciton

A Bound Electron-Hole Pair

The **electron and hole pair** can be generated by, for instance, photon absorption.

If they occupy conduction and valence edges, respectively, they are **spatially delocalized** and **move independently from each other**.

However, because of opposite charges, they attract and orbit around each other, and can form *a more stable bound state*. This is called the *exciton*.

- **Free to move together through the crystal.**

- **Weakly bound, with an average electron-hole distance large in comparison with the lattice constant.**

c

Conduction band

$n = \infty$
$n = 3$
$n = 2$
Exciton levels
$n = 1$

exciton

v

Valence band

e

h
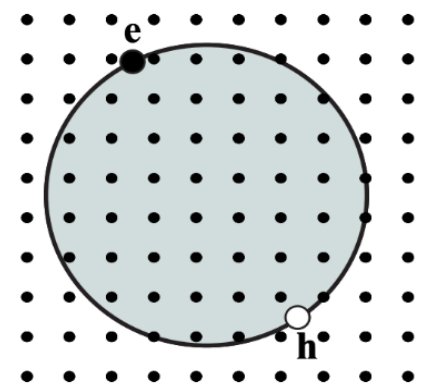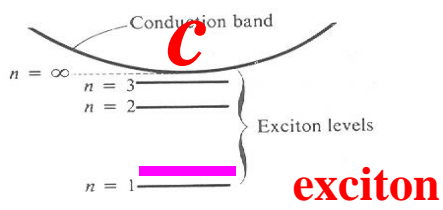
Exciton

Since the electron-hole separation is so large, it is a good approximation to average over the detailed structure of the atoms in between the electron and hole, and consider the particles to be moving in a **uniform dielectric material**. We can then model the free exciton as a **hydrogen-like system**. We just need two modifications: first, the electron-hole pair interacts within the dielectric medium so the static dielectric constant ($\varepsilon_r = \varepsilon^0$) is used. Second, unlike the proton, the effective mass of hole is similar to that of electron, so the **reduced mass (μ)** should be used.

$$\frac{1}{m} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

~25 meV   ~5 nm

$$E_{H,n} = -\frac{me^4}{8e_o^2 h^2 n^2} = -\frac{R_H}{n^2} = -\frac{13.6}{n^2}\text{eV} \quad \text{(Hydrogen atom)}$$

$$E_{ex,n} = -\frac{me^4}{8e_r^2 e_o^2 h^2 n^2} = -\frac{m}{m}\frac{1}{e_r^2}\frac{R_H}{n^2} = -\frac{R_X}{n^2} \quad \textbf{(Exciton)}$$

Crystal	E_g (eV)	R_X (meV)	a_X (nm)
GaN	3.5	23	3.1
ZnSe	2.8	20	4.5
CdS	2.6	28	2.7
ZnTe	2.4	13	5.5
CdSe	1.8	15	5.4
CdTe	1.6	12	6.7
GaAs	1.5	4.2	13
InP	1.4	4.8	12
GaSb	0.8	2.0	23
InSb	0.2	(0.4)	(100)

The size of exciton is calculated from the orbital size in the hydrogen

$$r_n = \frac{m}{m}e_r n^2 a_0 = n^2 a_X$$

Since the **exciton binding energy is very small** for Wannier exciton, it easily break at room temperatures.

Example)

(i) Calculate the exciton Rydberg energy and Bohr radius for GaAs, which has $\epsilon_r = 12.8$, $m_e^* = 0.067m_0$ and $m_h^* = 0.2m_0$.

(ii) GaAs has a cubic crystal structure with a unit cell size of 0.56 nm. Estimate the number of unit cells contained within the orbit of the $n = 1$ exciton. Hence justify the validity of assuming that the medium can be treated as a uniform dielectric in deriving eqns 4.1 and 4.2.

(iii) Estimate the highest temperature at which it will be possible to observe stable excitons in GaAs.

Solution

(i) We first need to calculate the reduced electron-hole mass μ, which is given by eqn 3.22. With $m_e^* = 0.067m_0$, and $m_h^* = 0.2m_0$, we find

$$\mu = \left(\frac{1}{0.067m_0} + \frac{1}{0.2m_0} \right)^{-1} = 0.05m_0 \,.$$

We then insert this value of μ and $\epsilon_r = 12.8$ into eqns 4.1 and 4.2 to obtain:

$$R_X = \frac{0.05}{12.8^2} \times 13.6 \,\text{eV} = 4.2 \,\text{meV} \,,$$

and

$$a_X = \frac{12.8}{0.05} \times 0.0529 \,\text{nm} = 13 \,\text{nm} \,.$$

(ii) We see from eqn 4.2 that the radius of the $n = 1$ exciton is equal to a_X. The volume occupied by this exciton is $\frac{4}{3}\pi a_X^3$ which is equal to $9.2 \times 10^{-24} \,\text{m}^3$. The volume of the cubic unit cell is equal to $(0.56 \,\text{nm})^3 = 1.8 \times 10^{-28} \,\text{m}^3$. Hence the exciton volume can contain 5×10^4 unit cells. Since this is a large number, the approximation of averaging the atomic structure to a uniform dielectric is justified.

(iii) The $n = 1$ exciton has the largest binding energy with a value of 4.2 meV. This is equal to $k_B T$ at 49 K. Therefore, we would not expect the excitons to be stable above ~ 50 K.
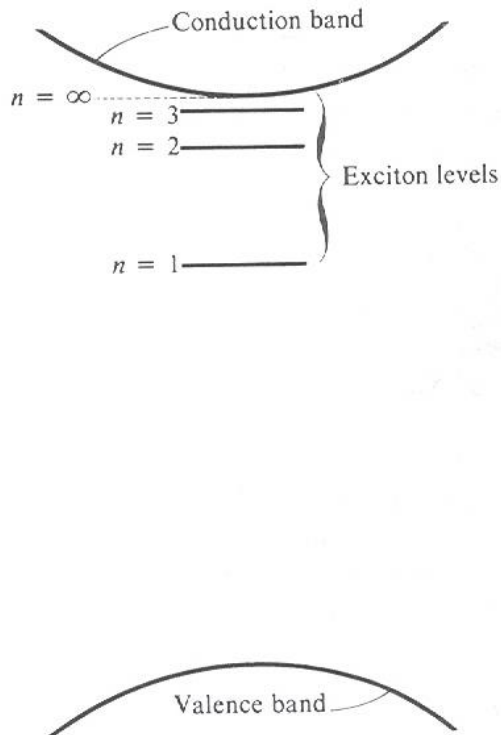
Excitons exhibiting just below the bandgap energy.

Absorption edge at 21 K

E_g = **1.521 eV** at **21 K**

Fig. 4.3 Excitonic absorption of GaAs between 21 K and 294 K. The dashed line is an attempt to fit the absorption edge using eqn 3.25 with a value of E_g equal to 1.425 eV, which is appropriate for GaAs at 294 K. After Sturge (1962), © American Physical Society, reprinted with permission.

64
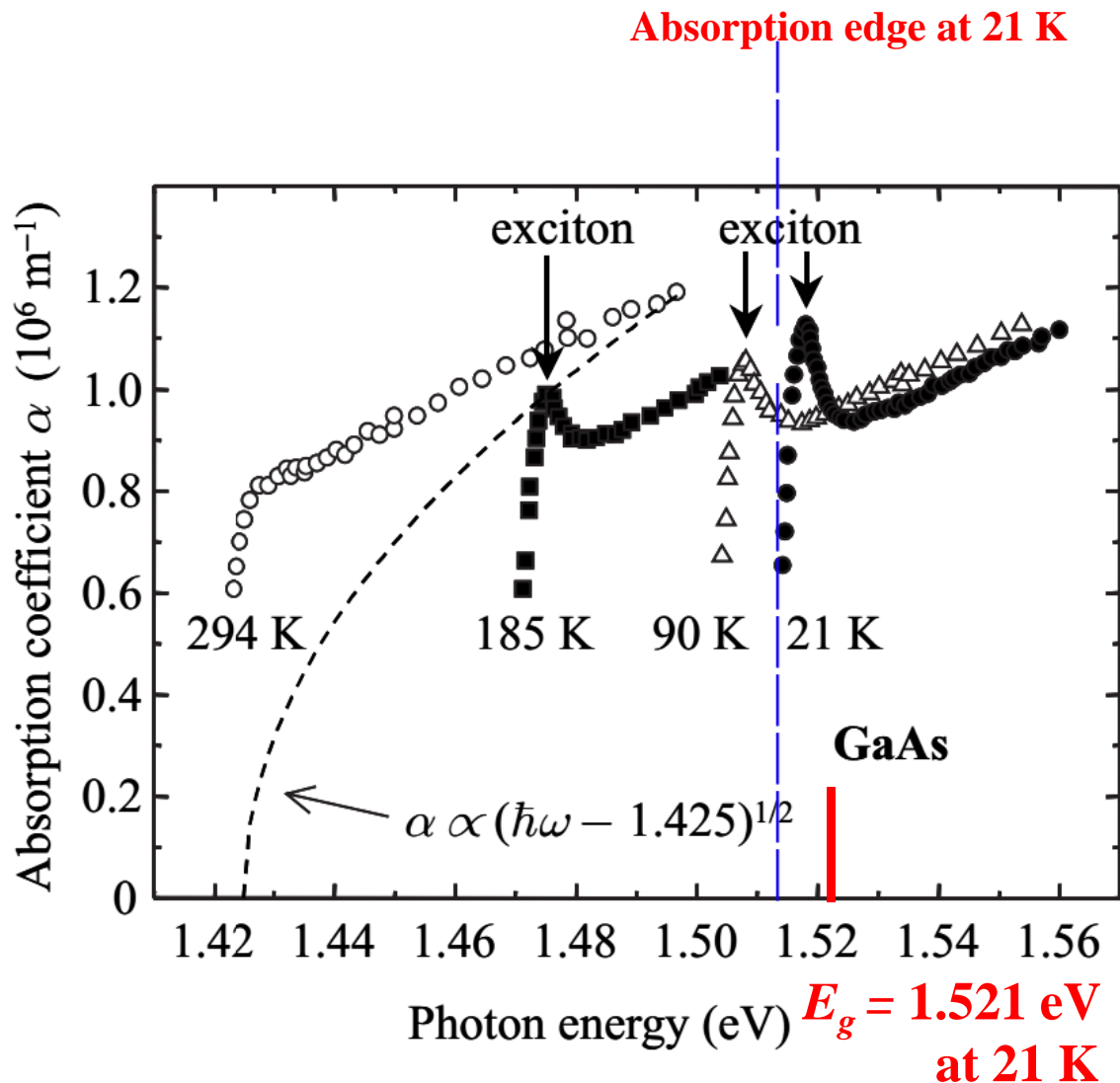
- ## **Miscellaneous Discussion**
  For the exciton to be formed, the electron and hole should have similar group velocities. If not, the exciton will break instantly because electron and hole move in different directions. This means that the exciton forms stably at the **k** point where the valence and conduction bands have similar slopes. In the typical band structure shown in the below, this happens only at the band edge points (typically **k** = 0).
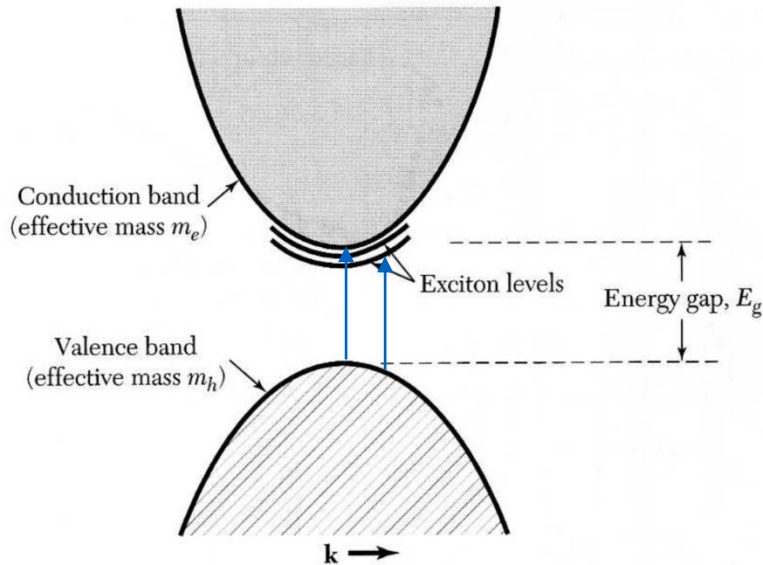
The exciton is also a kind of (quasi)particle so it can move freely in the lattice. The energy levels in the previous slide assume that the kinetic energy of exciton is zero. If we add the kinetic energy to these stationary exciton levels,

$$E = \frac{\hbar k_{ex}^2}{2(m_e^* + m_h^*)} + E_{ex,n}$$

which results in curved exciton levels shown in the left.

These dispersive exciton levels are also responsible for the enhanced absorption right above the absorption edge compared to the pure interband transition (see the dashed vertical arrow in the previous slide); the transition to this moving exciton is more probable because of the large wavefunction overlap (see vertical arrows in the above figure).

Frenkel exciton

In large band gap materials with small dielectric constants and large effective masses, the exciton radius becomes comparable to the interatomic spacing. In these materials, we observe small-size Frenkel excitons rather than Wannier excitons. The binding energy ranges from 0.1 eV to several eVs, and so the exciton is stable at room temperatures. Excitons in alkali halides belong to the Frenkel exciton.

Frenkel excitons can also be observed in many molecular crystals and organic thin film structures. On the right is the absorption spectrum of pyrene ($C_{16}H_{10}$) single crystals at room temperature. The excitons in molecular solids are important in the OLED technology.

The exciton effects become more pronounced for low dimensional materials such as quantum dot in which the Coulomb interaction between electron and hole is less screened than 3D materials.
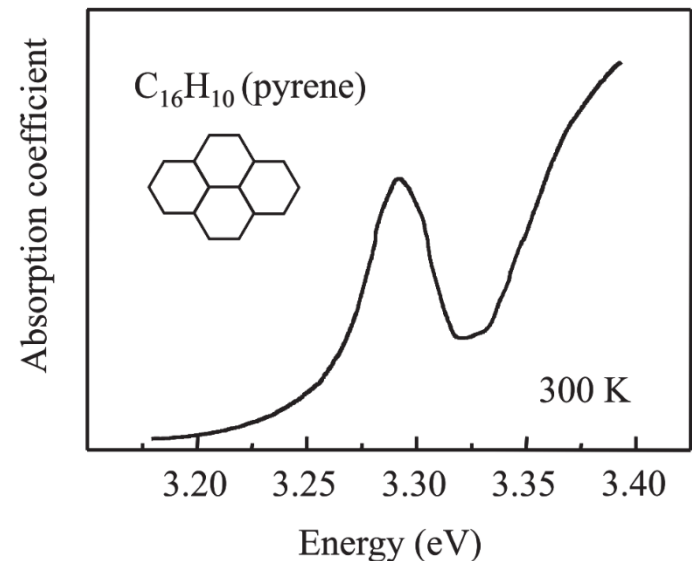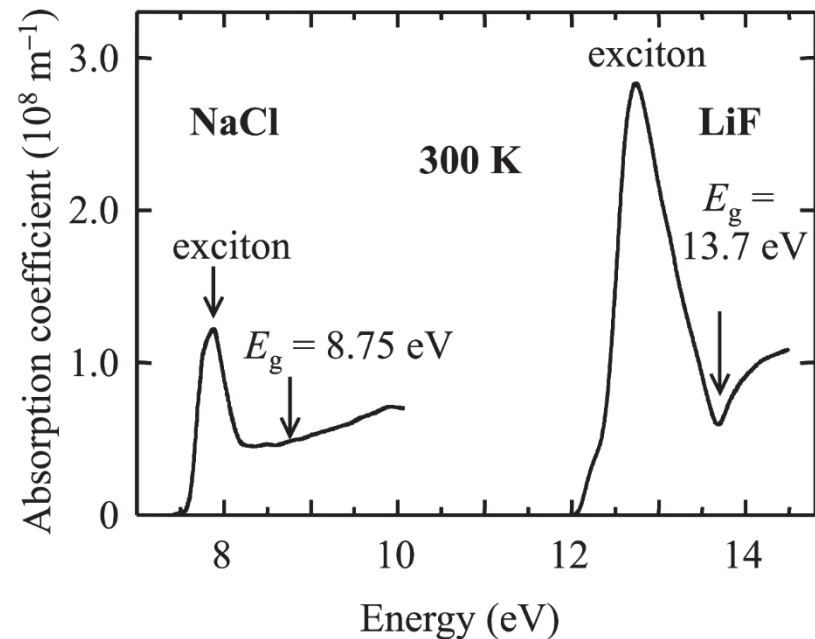
4C.4. Free Carrier Absorption

In doped semiconductors, the free carriers in the conduction or valence bands can absorb the photons, undergoing **intraband transitions with higher (photon) kinetic energies**. In order to conserve the momentum, this process should involve phonon generation or creation.

$$E = \frac{\hbar k^2}{2m_c^*}$$
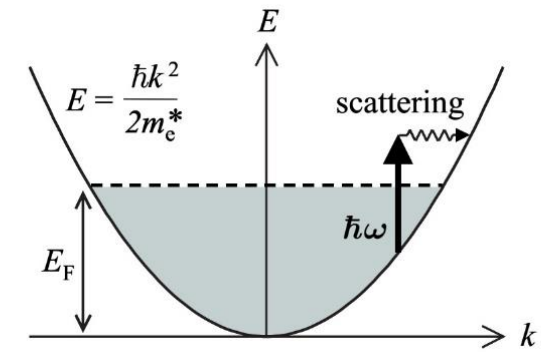
Absorption Edge (E_g = 1.43 eV = 0.87 μm)
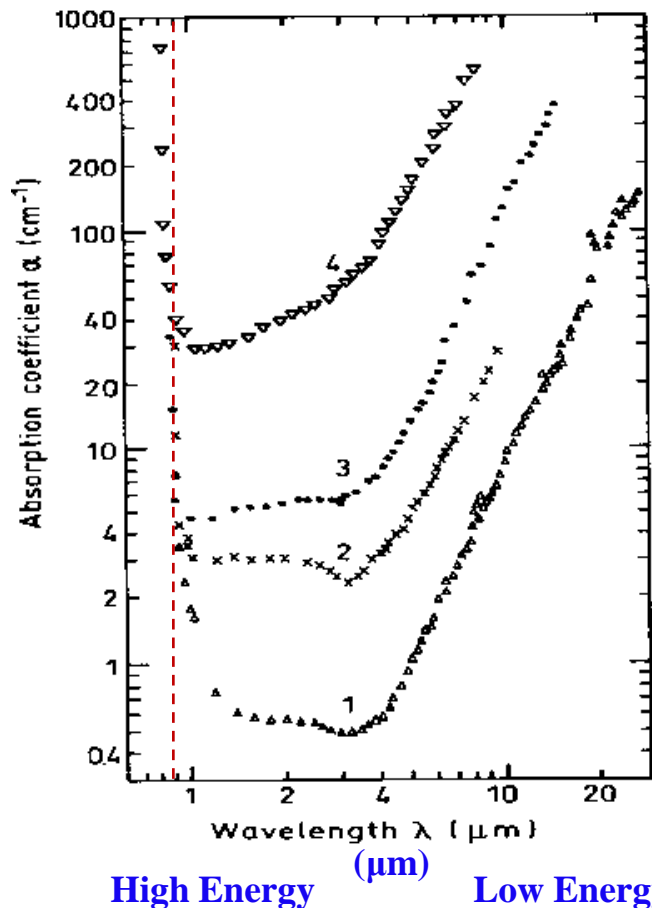
Free carrier absorption of GaAs vs. wavelength at different doping levels, 296 K. Conduction electron concentrations are:

1) $1.3 \times 10^{17} cm^{-3}$
2) $4.9 \times 10^{17} cm^{-3}$
3) $1.0 \times 10^{18} cm^{-3}$
4) $5.4 \times 10^{18} cm^{-3}$

The free carrier absorption occurs at IR region.

TCO
Transparent Conducting Oxide

$n \approx 5.0 \times 10^{20}$ **carriers/cm^3**
c-Si = 5.0×10^{22} **atoms/cm^3**

High Energy   (μm)   **Low Energy**

67

Transparent Conducting Oxide (TCO)

Optical and electronic properties of post-annealed ZnO:Al thin films

Yumin Kim, Woojin Lee, Dae-Ryong Jung, Jongmin Kim, Seunghoon Nam, Hoechang Kim, and Byungwoo Park[a]

Department of Materials Science and Engineering and Research Center for Energy Conversion and Storage, Seoul National University, Seoul 151-744, Republic of Korea

This study examined the optical and electronic properties of post-annealed Al-doped ZnO (ZnO:Al) thin films. The lowest resistivity was observed after annealing a sputter-deposited ZnO:Al film at 350 °C. X-ray photoelectron spectroscopy revealed a ~0.4 eV shift in the Fermi level when the carrier concentration was increased to 1.6×10^{20} cm^{-3} by Al doping and annealing. The optical band gap increased from 3.2 eV for insulating ZnO to 3.4 eV for conducting ZnO:Al, and was associated with conduction-band filling up to ~0.4 eV in a renormalized band gap. Schematic band diagrams are shown for the ZnO and ZnO:Al films. © 2010 American Institute of Physics.
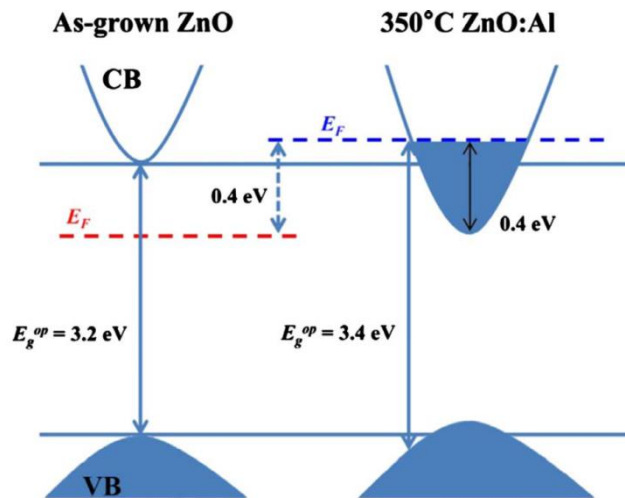
4C.5. Surface Plasmon

We have seen that free electrons oscillate with characteristic frequency called the plasma frequency. According to quantum mechanics, the energy of plasma oscillation is **quantized** like other waves, and each energy quanta is called the **plasmon**.

When the oscillation occurs inside the material, it is called **bulk plasmon**. As can be seen in the figure, the bulk plasma oscillation is **longitudinal**, so it couples with photon very weakly. (Imagine generating waves inside the water.)

If the charge oscillation occurs at the metal surface, like one we have seen in the plasma reflectivity, the energy quanta is called the **surface plasmon**. This surface wave can be **both longitudinal and transverse** (imagine making waves on the water surface). Therefore, the **surface plasmon can strongly couple with photon**, which leads to a number of interesting applications in **nanophotonics**. This field is called plasmonics.

− **Electron Rich**
+ **Ion Rich**

⟶ **Electric-Field Direction**

⟶ **Photon Direction**

k
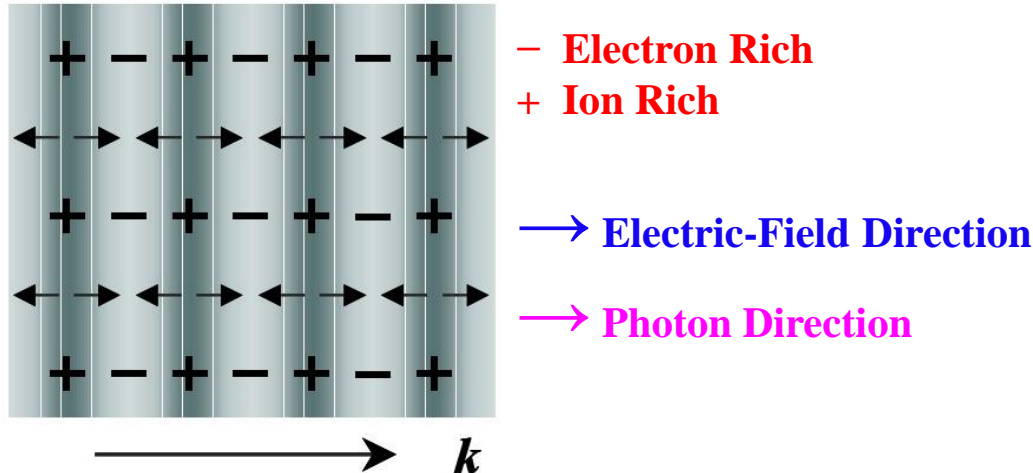
Bulk Plasmon
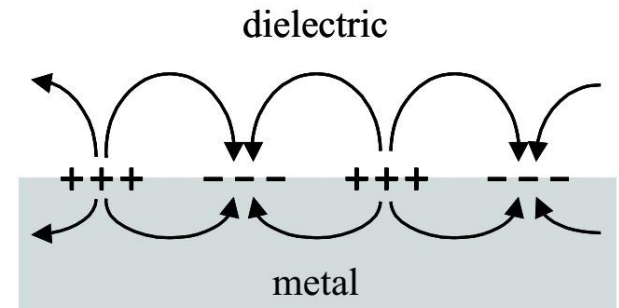
dielectric

metal

Surface Plasmon

Fig. 7.14 Electric fields associated with electron charge density fluctuations at the surface of a metal.

Nanophotonics
LED, Water Splitting, Solar Cells, etc.

Plasmonic Dye-Sensitized Solar Cells Using Core—Shell Metal—Insulator Nanoparticles

ABSTRACT: We present an investigation into incorporating core—shell Au—SiO$_2$ nanoparticles into dye-sensitized solar cells. We demonstrate plasmon-enhanced light absorption, photocurrent, and efficiency for both iodide/triiodide electrolyte based and solid-state dye-sensitized solar cells. Our spectroscopic investigation indicates that plasmon-enhanced photocarrier generation competes well with plasmons oscillation damping with in the first tens of femtoseconds following light absorption.

Plasmonic light harvesting antennae

light

Metal nanoparticle

TiO$_2$

Henry J. Snaith's Group
(Univ. of Oxford)
Nano Letters (2011)

4C.6. Raman Spectroscopy (= Reststrahlen Absorption)

The photons can interact with phonons. We have already discussed the classical version of photon-phonon interaction in the ionic polarization. For the quantitative discussion, one needs to elaborate on the detailed interactions mechanism between IR-active lattice oscillations and electromagnetic waves which is beyond the current scope.

In a quantum picture, the interaction is collision process **between photon and phonon**. Like electron-photon collision, the energy and momentum should be conserved. This leads to the selection rule within the phonon dispersion. It is seen that **only optical branch can interact with the photon** in order to conserve both energy and momentum. (Light is much faster than any sound wave!)

Since the interaction occurs mainly near the zone center with the energy of IR photon, the particle nature is not so strong in photon-phonon interaction and the classical picture gives good account of most absorption spectrum.

Phonon Dispersion
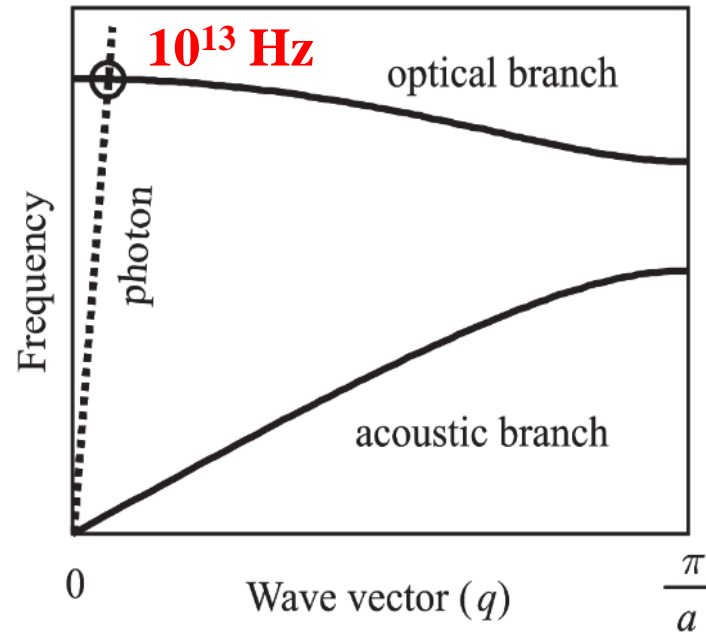
10^{13} **Hz**

optical branch

photon

Frequency

acoustic branch

0

Wave vector (q)

$\dfrac{\pi}{a}$

4D. Quantum Phenomena: Luminescence

In semiconductors, the electron-hole pair generated by the photon absorption entails other interesting phenomena, which are called optoelectronic effects. In semiconductors, the electron-hole pair increases the carrier density and results in the increase in conductivity, which is called **photoconductivity**. The photoconductivity is exploited in detecting the photon of certain frequencies (**photo detector**).

The electron-hole pairs are eventually annihilated such that the system goes back to the original equilibrium state. If this relaxation is achieved by emitting a photon, the radiative emission process is called **luminescence**. (This is like atoms emit light by spontaneous emission when electrons in excited states drop down to a lower level by radiative transitions.) The luminescence is used in various optoelectronic devices, most notably light-emitting diodes (**LEDs**).

The physical processes involved in luminescence are more complicated than those in absorption. This is because the generation of light by luminescence is intimately tied up with the **energy relaxation mechanisms in the solid**.

We first discuss on the **spontaneous emission** in which electron-hole pair recombine spontaneously without stimuli from ambient photons. (It is like emission in the dark room.)

When the photon density or light intensity is very high, the **stimulated emission** becomes significant, which is used in **laser**.

-Tue/Nov/17/2020

4D.1. General Discussion
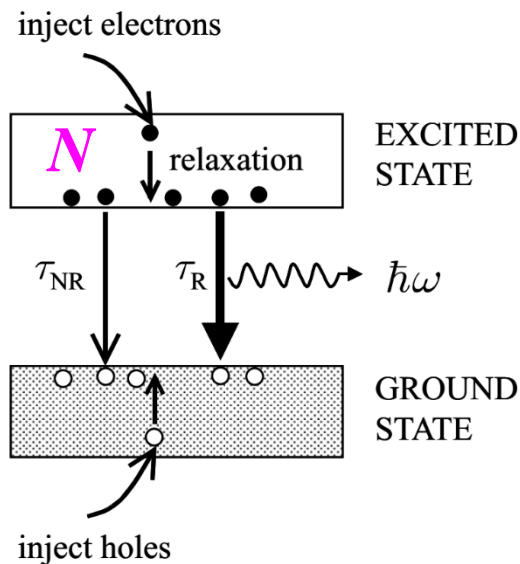
When N electrons are excited into higher energy states, they recombine with holes in lower energy states through various mechanisms with certain rates. For the **radiative decay processes**, the number changes according to the following differential equation.

$$\left(\frac{dN}{dt}\right)_{\text{radiative}} = -AN$$

Here A corresponds to the transition rate. The solution is

$$N(t) = N(0)\exp(-At) = N(0)\exp(-t/\tau_R)$$

$$\boldsymbol{\tau_R}$$

radiative lifetime = [radiative recombination rate]$^{-1}$

There exist **nonradiative processes** that also lead to the decay of electron-hole pairs. If $1/\tau_{NR}$ is the **nonradiative recombination rate** for these processes,

$$\left(\frac{dN}{dt}\right)_{\text{total}} = -\frac{N}{\tau_R} - \frac{N}{\tau_{NR}} = -N\left(\frac{1}{\tau_R} + \frac{1}{\tau_{NR}}\right)$$

The **luminescence efficiency (quantum efficiency)** is the ratio of the photon number to the total number of excited electrons:

$$\eta_R = \frac{AN}{N(1/\tau_R + 1/\tau_{NR})} = \frac{1}{1 + \tau_R/\tau_{NR}}$$

Number Efficiency

Not the Energy Efficiency

(in solar cell, energy efficiency)

73

Nonradiative Recombination

Electron-hole pairs can also recombine through nonradiative procedures.

Trap-Assisted Recombination:

The trap is a defect level that forms deep inside the bandgap. It is caused by defects such as vacancies, interstitials, grain boundaries, dislocations, or external defects like dopants. Unlike shallow levels, it is highly localized over **only a few atomic sites**. Since the **translational symmetry is broken** near the defect site, **any k state can drop to the trap**. The transition into the deep level is dominantly mediated by **emission of phonons**.

Besides the nonradiative decay, the trap can also act as the **carrier trapping center**, degrading the **electrical conductivity σ (or mobility μ)**.

E_t

trap-assisted recombination

Nonradiative Recombination

CB
E_c
E_r Recombination center
E_v
VB

E_r

E_r Phonons

(a) Recombination

CB
E_c
E_t Trapping center
E_v
VB

E_t

E_t

Trapped   **Detrapping**
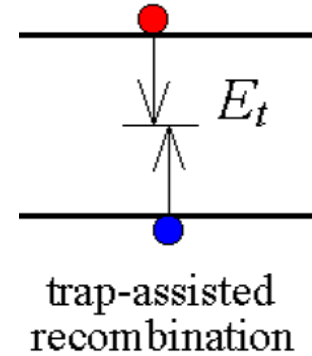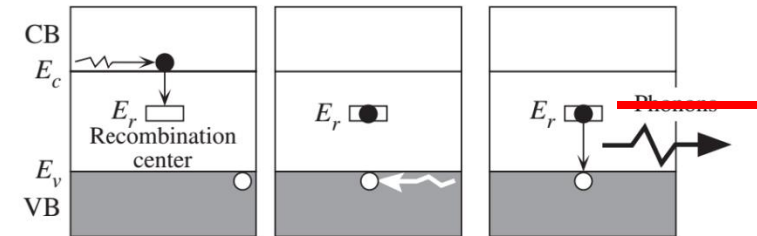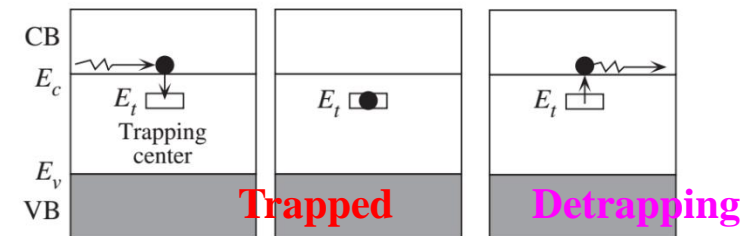
(b) Trapping

4D.2. Interband Luminescence

When an electron in one band and hole in another band recombine and emits a photon, it is called interband luminescence. This is reverse of the interband absorption.

Since the momentum of the photon is negligible compared to the momentum of the electron, the electron and hole that recombine must **have the same k vector**, like in absorption process.

Therefore, the optical transition between the valence and conduction bands of **typical direct gap semiconductors** occur with high probabilities. The **radiative lifetime will be short**, with typical values in the range 10^{-8} ~10^{-9} s. The interband luminescence is also called the electron-hole recombination.

Direct gap

In the case of **indirect semiconductor**, the radiative decay should be accompanied by phonon that conserve the momentum. Like absorption, this process is highly inefficient with **long τ_R**. Instead they can recombine through traps, just producing phonons. This is why indirect-gap material such as Si is not used in the optoelectronic applications. Instead III-V compound semiconductor is widely used.

Indirect gap
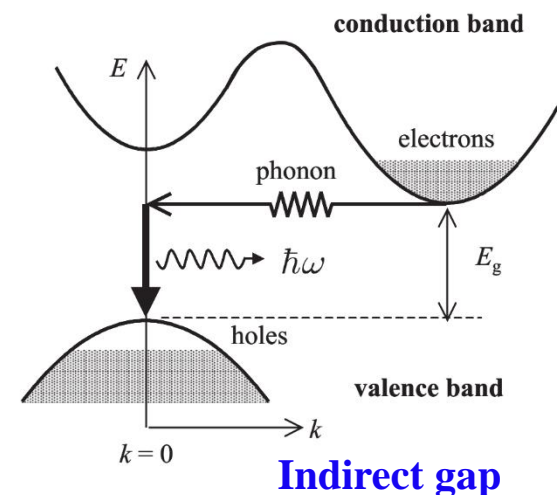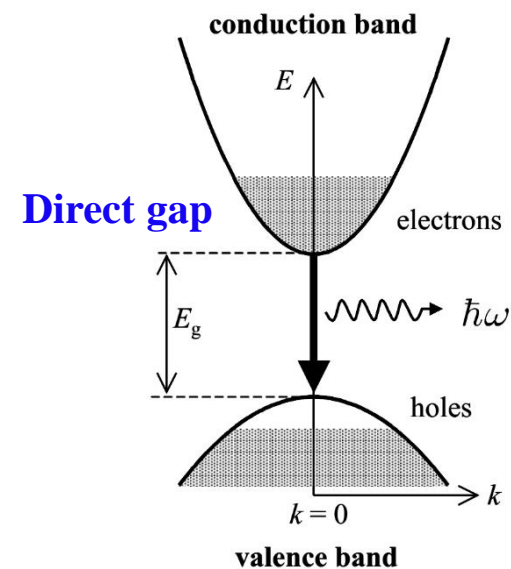
Radiative Recombination Rate = [Radiative Lifetime]$^{-1}$

Nonradiative Recombination Rate = [Nonradiative Lifetime]$^{-1}$

Example)

The band gap of the III–V semiconductor alloy $Al_xGa_{1-x}As$ at $k = 0$ varies with composition according to $E_g(x) = (1.420 + 1.087x + 0.438x^2)$ eV. The band gap is direct for $x \leq 0.43$, and indirect for larger values of x. Light emitters for specific wavelengths can be made by appropriate choice of the composition.

(a) Calculate the composition of the alloy in a device emitting at 800 nm.

(b) Calculate the range of wavelengths than can usefully be obtained from an AlGaAs emitter.

Solution

(a) The photons at 800 nm have an energy of 1.55 eV. The device will emit at the band gap wavelength, so we must choose x such that $E_g(x) = 1.55$ eV. On substituting into the relationship for $E_g(x)$, we find $x = 0.11$.

(b) The long wavelength limit is set by the smallest band gap that can be obtained in the alloy, namely 1.420 eV for $x = 0$. The short wavelength limit is set by the largest direct band gap that can be obtained, namely 1.97 eV for $x = 0.43$. The useful emission range is therefore 1.42–1.97 eV, or 630–870 nm. Alloy compositions with $x > 0.43$ are not useful because indirect gap materials have very low luminescent efficiencies.

Photoluminescence

Photoluminescence (PL) means the reemission of light after absorbing a photon of **higher energy**.

The **electron–phonon coupling in most solids is very strong** and these scattering events take place on time scales as short as ~ 100 fs (i.e. $\sim 10^{-13}$ s). This is much **faster than the radiative lifetimes** which are in the nanosecond range, and the **electrons are therefore able to relax to the bottom of the conduction band** long before they have had time to emit photons.

The same conditions apply to the **relaxation of holes** in the valence band.

Therefore, while the absorption occurs over the broad energy range higher than energy gap, **PL is peaked at around the bandgap**.
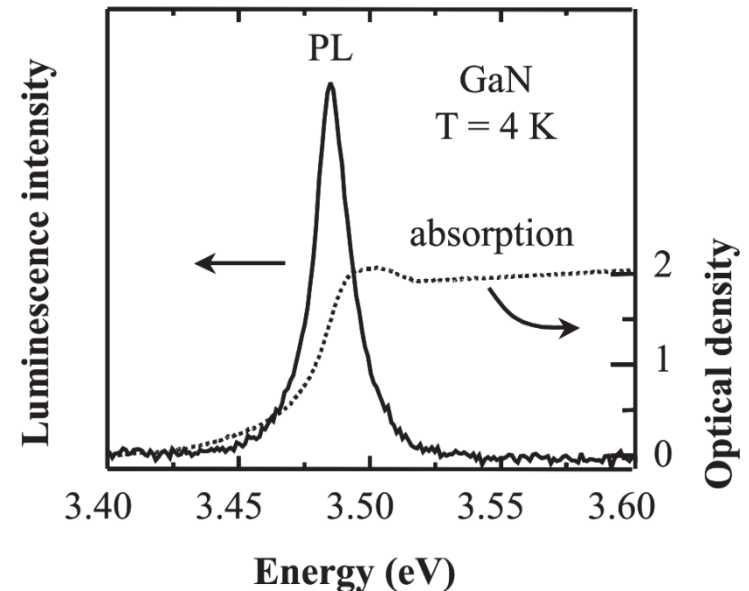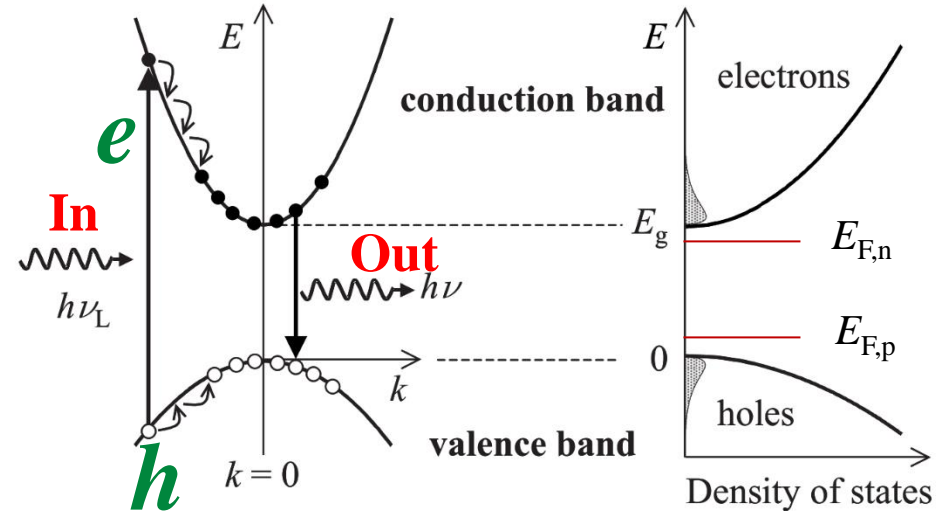
Since electrons and holes are thermally equilibrated by phonons, their distribution follows the Fermi-Dirac distribution within their bands under the separate Fermi levels, so called **quasi Fermi level**. In the previous slide, $E_{F,n}$ and $E_{F,p}$ are the quasi Fermi levels for electron and hole, respectively. The mass action law does not hold in this non-equilibrium condition.

When the extra carriers are not too much (the external light is weak), the distribution of electrons and holes before the emission follow the Boltzmann distribution with separate quasi Fermi levels. The luminescence intensity is then given by:

$$I(h\nu) \propto (h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu - E_g}{k_B T}\right)$$

Thus, the spectrum rises sharply at E_g and then falls off exponentially with a decay constant of kT due to the Boltzmann factor. We thus expect a sharply peaked spectrum of width $\sim kT$ starting at E_g. This is confirmed by PL spectrum in GaAs in the right.
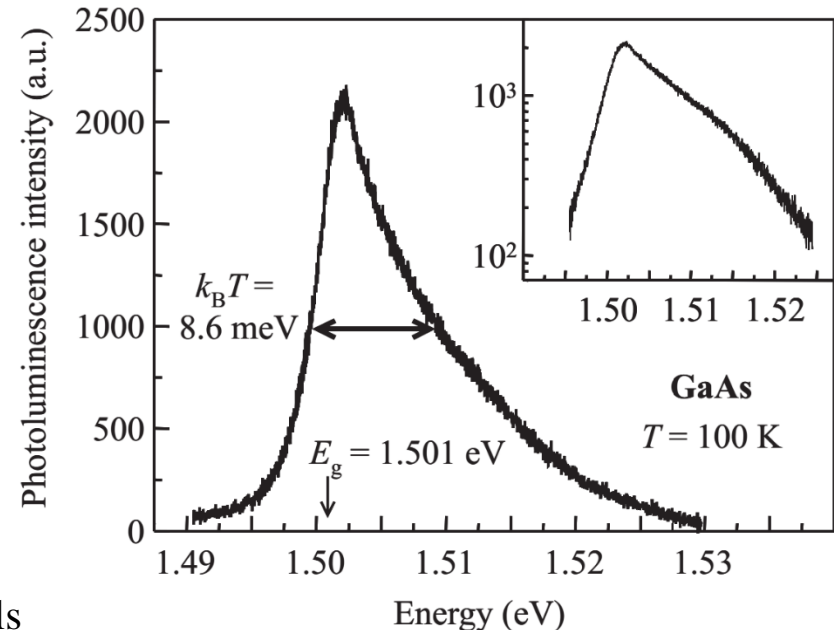
Depletion Layer   *p-n* **Junction**

Figure 29.3

(a) Carrier densities, (b) charge density, and (c) potential $\phi(x)$ plotted vs. position across an abrupt *p-n* junction. In the analysis in the text the approximation was made that the carrier densities and charge density are constants except for discontinuous changes at $x = -d_p$ and $x = d_n$. More precisely (see Problem 1), these quantities undergo rapid change over regions just within the depletion layer whose extent is a fraction of order $(k_B T/E_g)^{1/2}$ of the total extent of the depletion layer. The extent of the depletion layer is typically from 10^2 to 10^4 Å.

$$\nabla \cdot D = 4\pi\rho$$
$$D = \varepsilon E$$
$$E = -\nabla \Phi$$

$$\rho\,(x)$$

$$\Phi\,(x)$$

Carrier Density at a p-n Junction

Figure 29.4

The charge density ρ and potential ϕ in the depletion layer (a) for the unbiased junction, (b) for the junction with $V > 0$ (forward bias), and (c) for the junction with $V < 0$ (reverse bias). The positions $x = d_n$ and $x = -d_p$ that mark the boundaries of the depletion layer when $V = 0$ are given by the dashed lines. The depletion layer and change in ϕ are reduced by a forward bias and increased by a reverse bias.
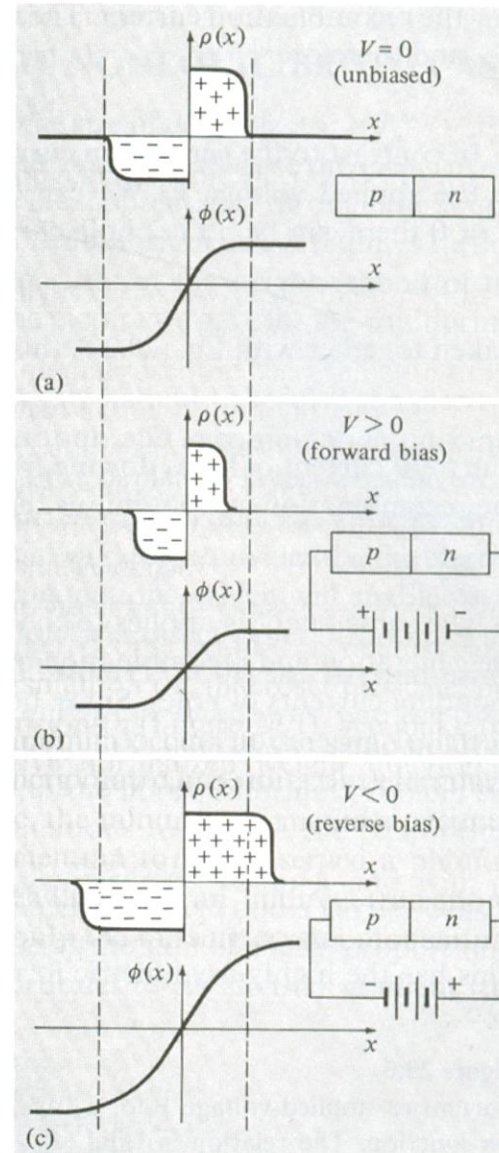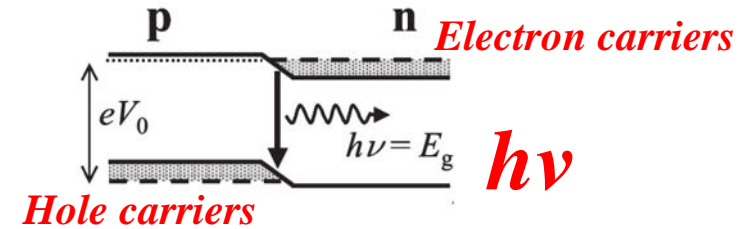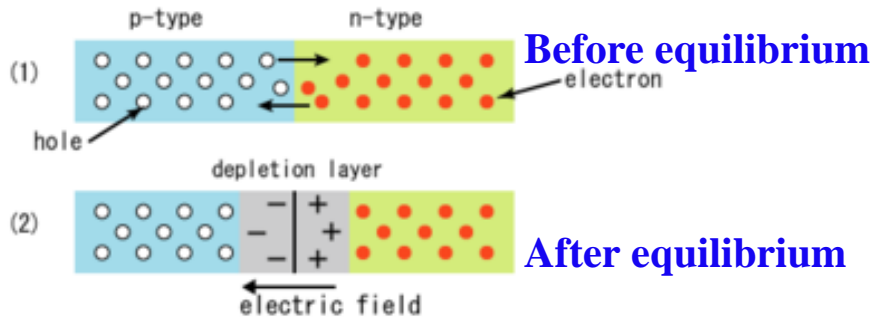

Equilibrium

Forward bias

Reverse bias

Ashcroft, Solid State Physics

Electroluminescence (*p-n* Junction)

Electroluminescence is the process by which luminescence is generated while an electrical current flows through an optoelectronic device. The light-emitting diodes (LEDs) based on the ***p-n* junction** are most well known.

Before equilibrium

After equilibrium

Built-in potential

$$E = -\nabla \Phi$$

$$V = 0$$

Electron carriers

$$h\nu$$

Hole carriers

$$V > 0$$

(b) $V_0 \approx +E_g/e$

When *p*-type and *n*-type semiconductors are joined seamlessly, the electrons and holes move, creating dipoles at the interface. This creates the electrostatic potential step and **adjust the Fermi level** in *p*-type and *n*-type region. At the interface, the **depletion layer is formed in which carriers are scarce**.

When a bias of E_g/e is applied, the electrons and holes diffuse to the depletion region. This creates a region in the junction where **both electrons and holes are present in the near (adjacent) spatial point**. As the electron and hole recombine through interband luminescence, **photons with the energy of E_g (approximately)** are emitted.
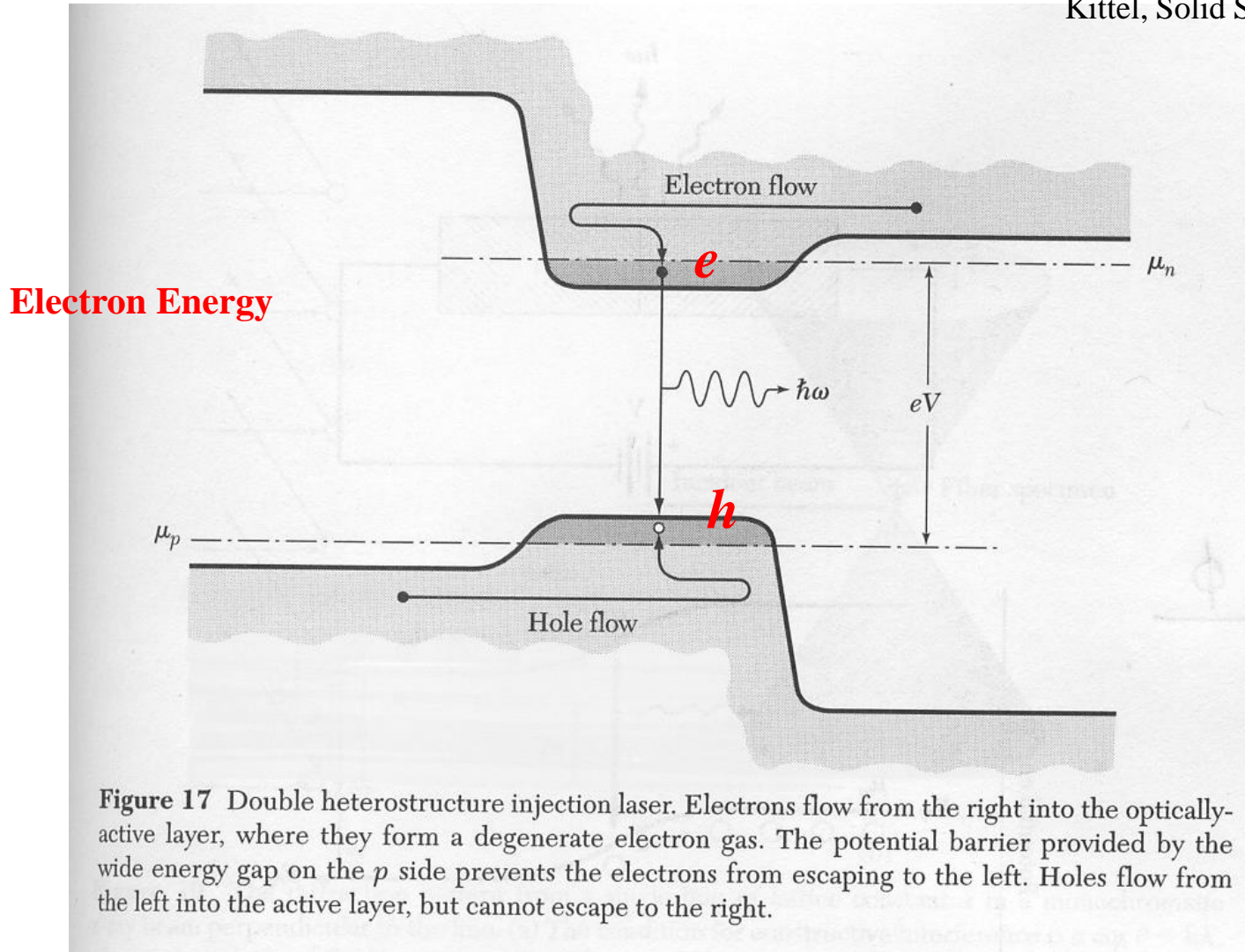
Electron-Hole Recombination of a p-n Junction

Kittel, Solid State Physics (Chapter 17).

Electron Energy

**Figure 18** Electron-hole recombination into photons, across a *p-n* junction.
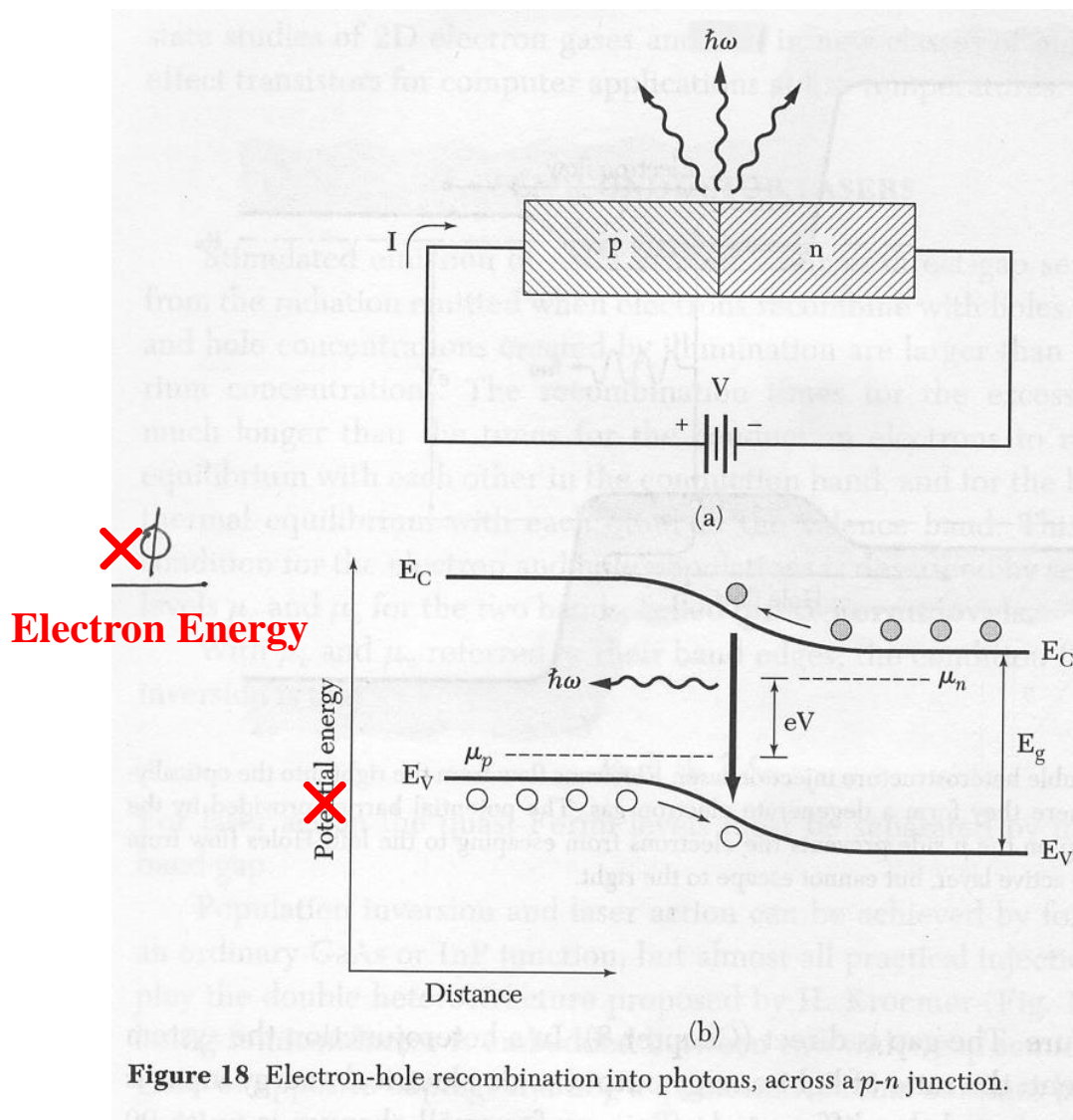
Double Heterostructure Injection Laser

Kittel, Solid State Physics (Chapter 17).

Electron Energy

Electron flow

e

μ_n

$\hbar\omega$

eV

h

μ_p

Hole flow

Figure 17 Double heterostructure injection laser. Electrons flow from the right into the optically-active layer, where they form a degenerate electron gas. The potential barrier provided by the wide energy gap on the p side prevents the electrons from escaping to the left. Holes flow from the left into the active layer, but cannot escape to the right.

Cathodoluminescence

Cathodoluminescence is the phenomenon by which light is emitted from a solid in response to excitation by cathode rays, that is electron beams (e-beams).

Cathodoluminescence is extensively used in cathode ray tubes, and it is also a powerful research tool. The basic processes occur when an e-beam strikes a crystal. The electrons in the e-beam are called **primary electrons**, and have an energy which is determined by the applied voltage, which might typically be 1-100 kV. The electrons that penetrate the surface transfer their energy to the crystal by **exciting electron-hole pairs**. These electrons and holes are created high up in their bands, and emit photons in all directions with energy of E_g after having relaxed to the bottom of their bands. It is these photons that comprise the cathodoluminescence signal.
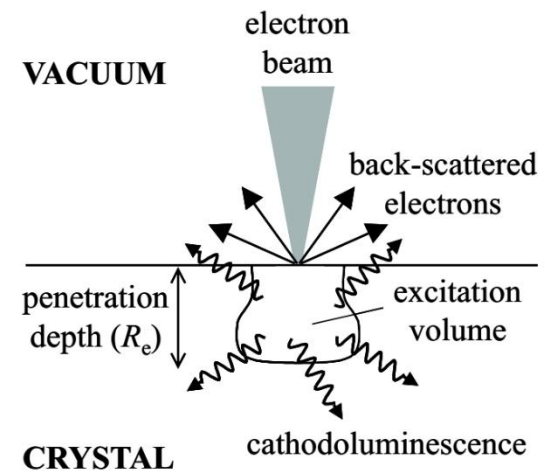
Cathodoluminescence

X-Ray Source for:
  Diffraction, Lithography, Tomography, etc.

One Electron In → Many Secondary Electrons Out
Secondary Electrons
  Scanning Electron Microscopy (SEM)

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4D.3. Luminescence Centers

In many materials, there are defects or **dopants that are optically active**. They are called the luminescence centers.

For example, the pure diamond is a wide bandgap material and so it is transparent and does not emit any light. However, when boron impurities are present, it becomes blue diamond. They are called as color centers.

Another example is the oxygen vacancy. ZnO has a bandgap of 3.4 eV so it should be transparent. However, depending on the amount of oxygen vacancies, it takes certain colors as shown in the right.
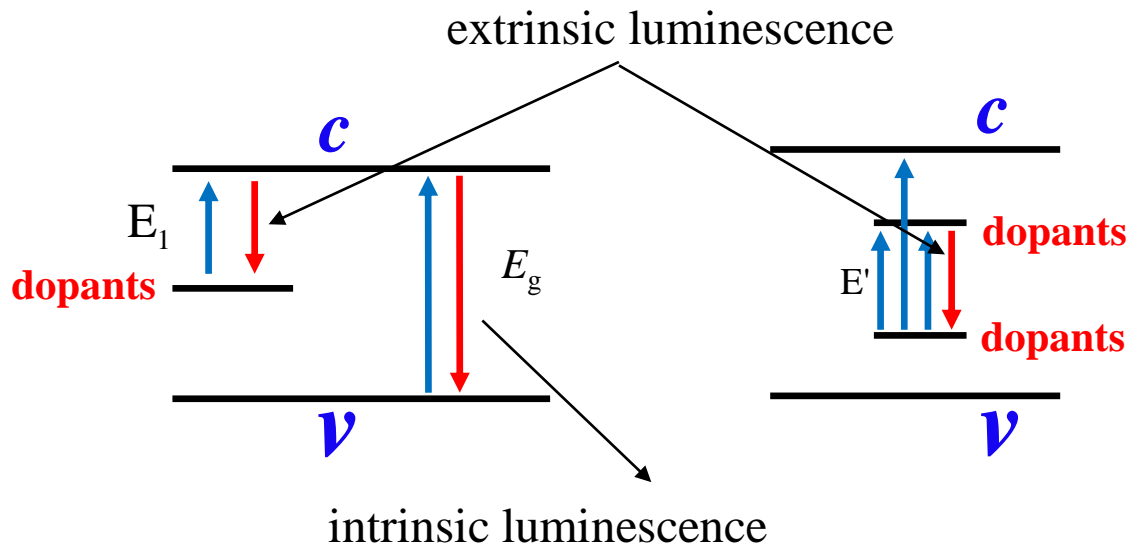
Jewelry

Synthetic ZnO crystals. Red and green are associated with different concentrations of oxygen vacancies.

Sapphire

extrinsic luminescence

intrinsic luminescence

In phosphors, various dopants are intentionally introduced in solids to emit photons at certain frequency.

4D.4. Stimulated Emission

So far, all the luminescence was spontaneous emission. While the electron in the conduction band waits for recombination with hole in the valence band for about nanoseconds, **if there are photons passing by, the recombination process is stimulated**. The resulting photon is **coherent (in phase)** with the ambient photons. This is called **stimulated emission**.
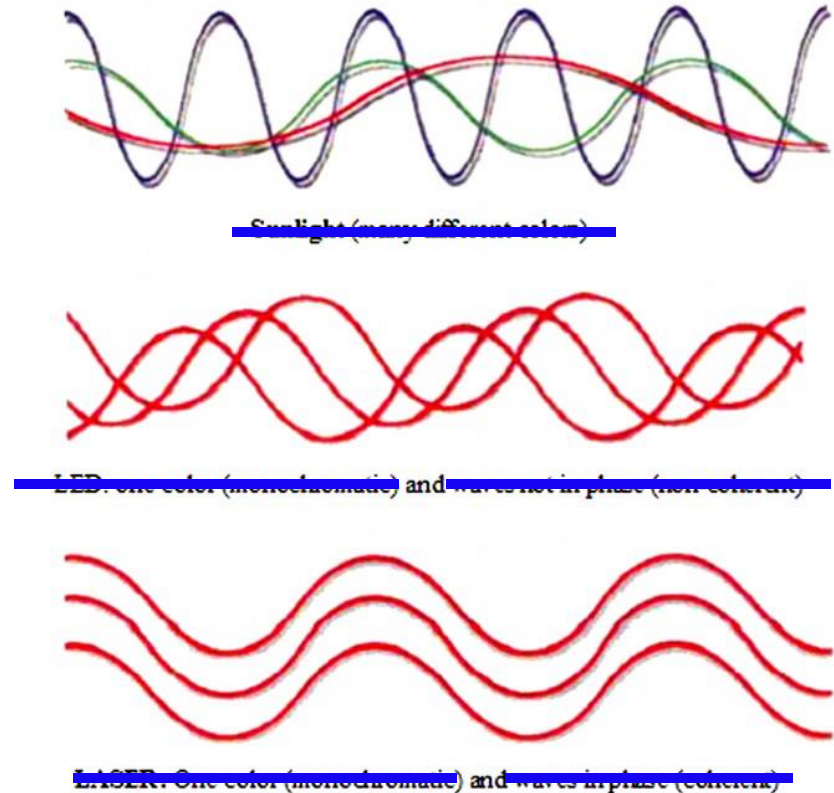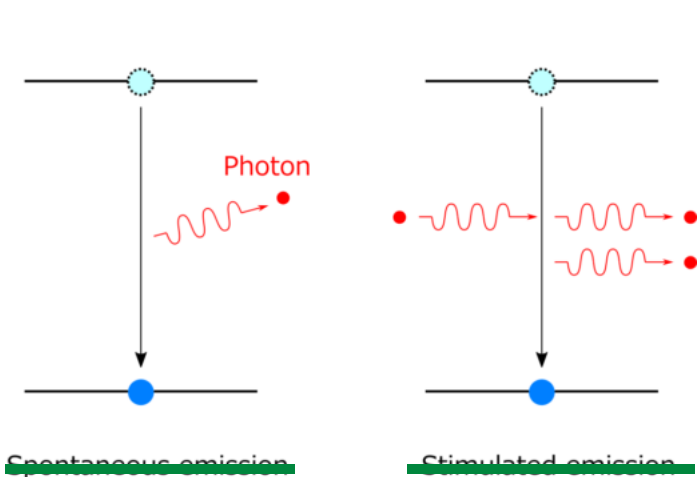
Such stimulated emission becomes **significant with increasing electron populations** in higher energy states. By increasing the current density in LED and optical mirrors **to confine photons**, one can make laser diode which performs better than LED. (The acronym ʻlaserʼ stands for ʻ**Light Amplification by Stimulated Emission of Radiation**ʼ.)

Why the laser is so strong? For spontaneous emission, there is a limit increasing the light intensity simply by increasing current density. In stimulated emission, the recombination can be enhanced by the ambient light.
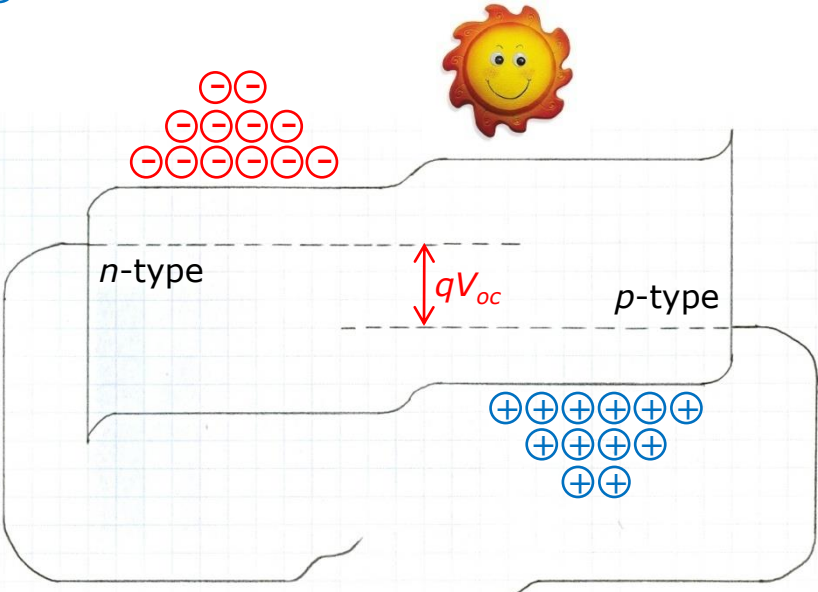
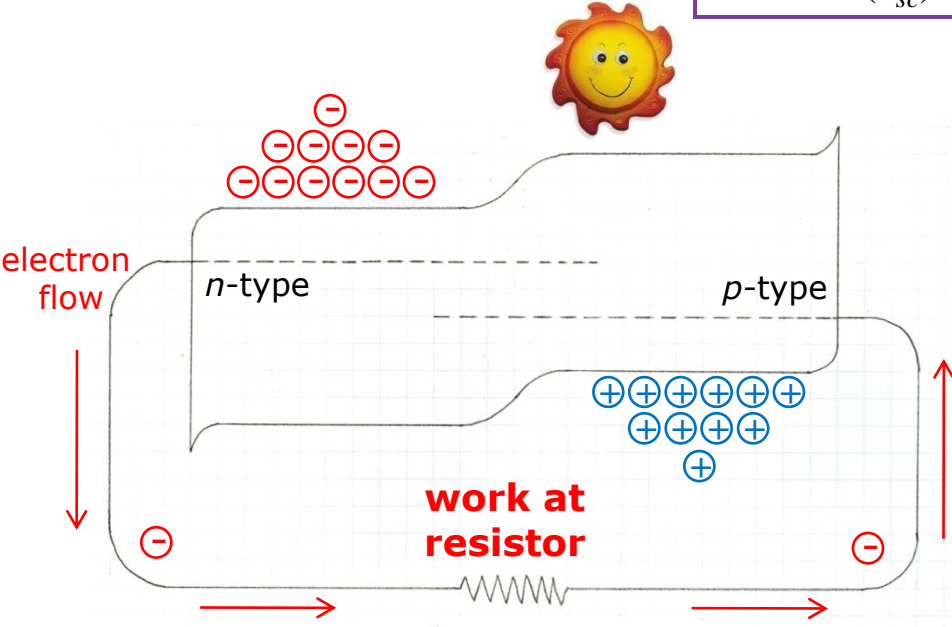# Energy Band of *p-n* Junction Solar Cell
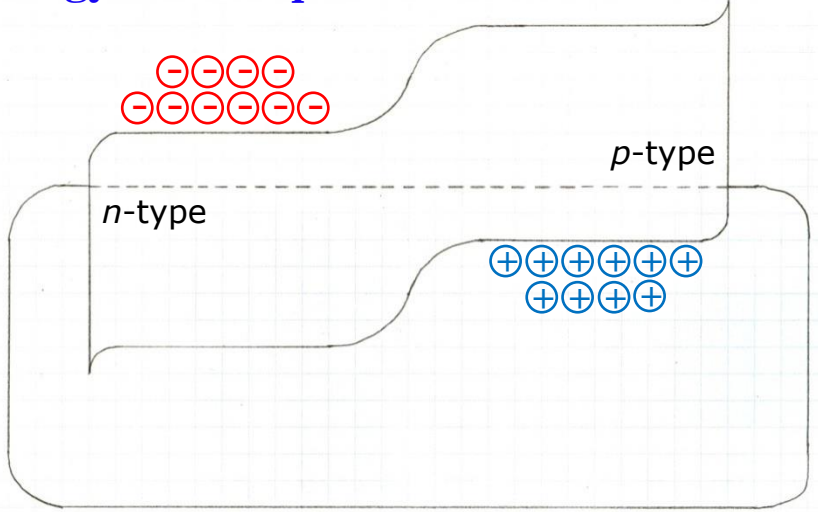
Dark Flux & 0 V

electron flow
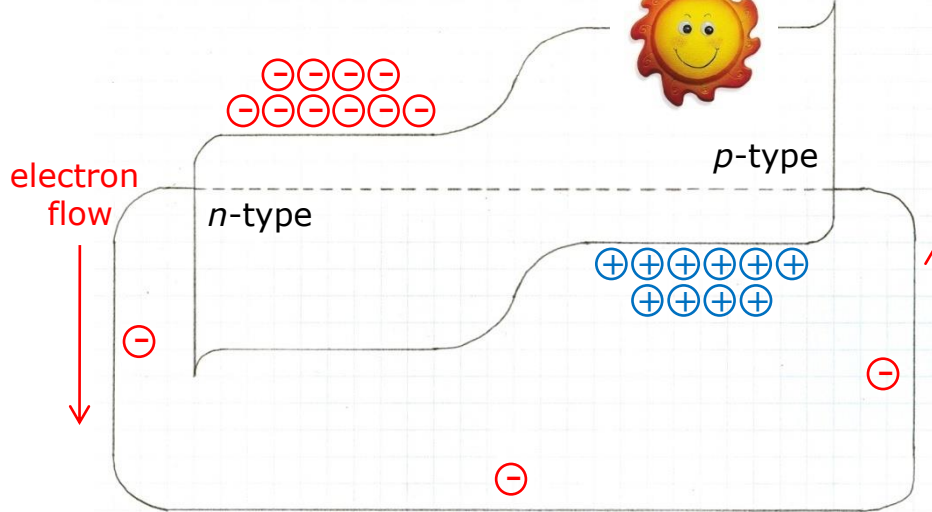
Short-Circuit Current (J_{sc})

$\ominus$: electron

$\oplus$: hole

qV_{oc}

Open-Circuit Voltage (V_{oc})

electron flow

work at resistor

Maximum Power Point (P_{max})

Solar Cell   Changwoo

Advantage of Quantum Dots

Tailoring Absorption (CdSe QDs)
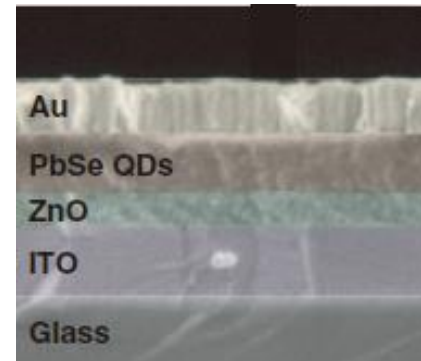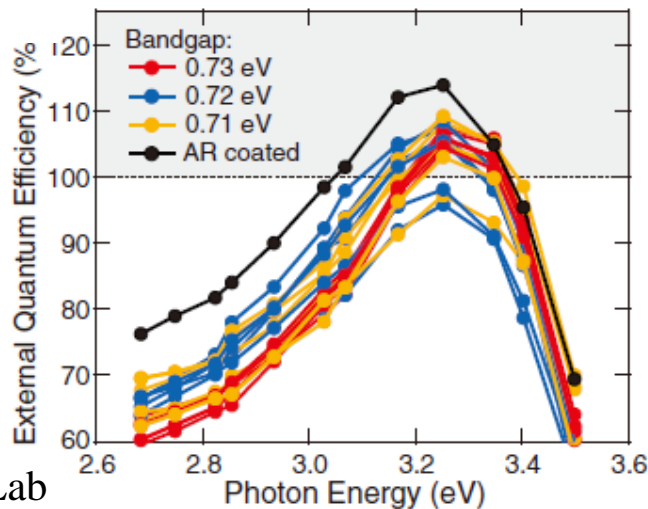

http://gizmodo.com
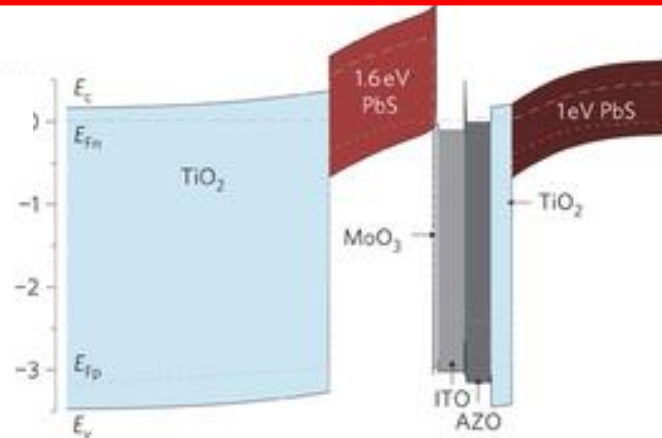
E.H. Sargent, University of Toronto (Canada)
Nature Photonics (2011).

Multiple-Electron Generation
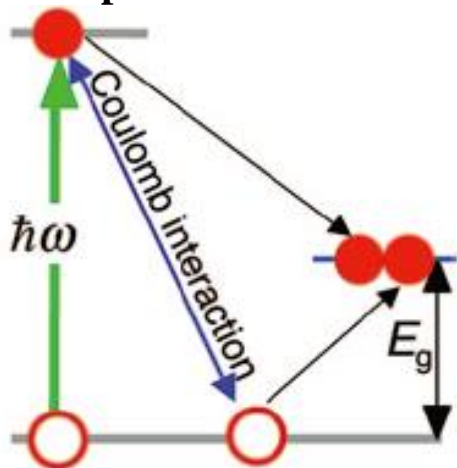
V. I. Klimov, Los Alamos National Lab
Nano Lett. (2008).

Nozik, NREL
Science (2011).

Solar Cell   Jongmin