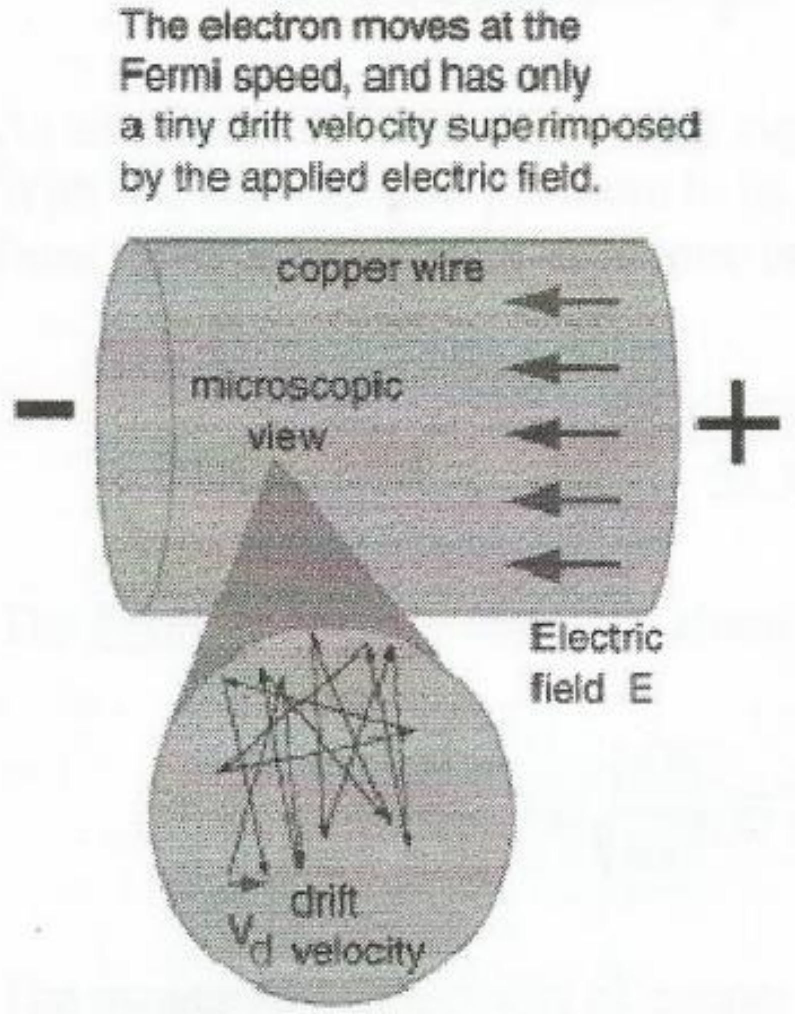
Ohm’s Law ~ 1870

Microscopic View of Ohm's Law



The electron moves at the Fermi speed, and has only a tiny drift velocity superimposed by the applied electric field.

When electric current in a material is proportional to the voltage across it, the material is said to be "ohmic", or to obey Ohm's law. A microscopic view suggests that this proportionality comes from the fact that an applied electric field superimposes a small drift velocity on the free electrons in a metal. For ordinary currents, this drift velocity is on the order of millimeters per second in contrast to the speeds of the electrons themselves which are on the order of a million meters per second. Even the electron speeds are themselves small compared to the speed of transmission of an electrical signal down a wire, which is on the order of the speed of light, 300 million meters per second.

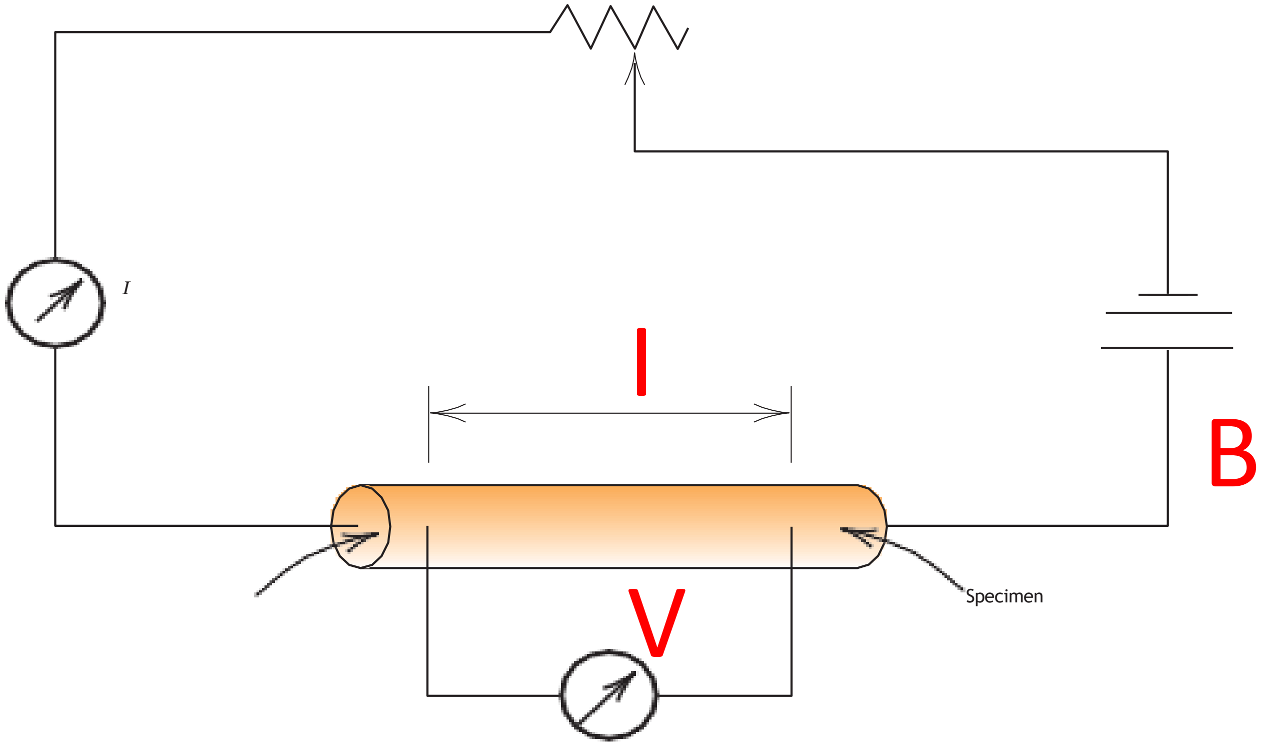
The current density (electric current per unit area, J=I/A) can be expressed in terms of the free electron density as

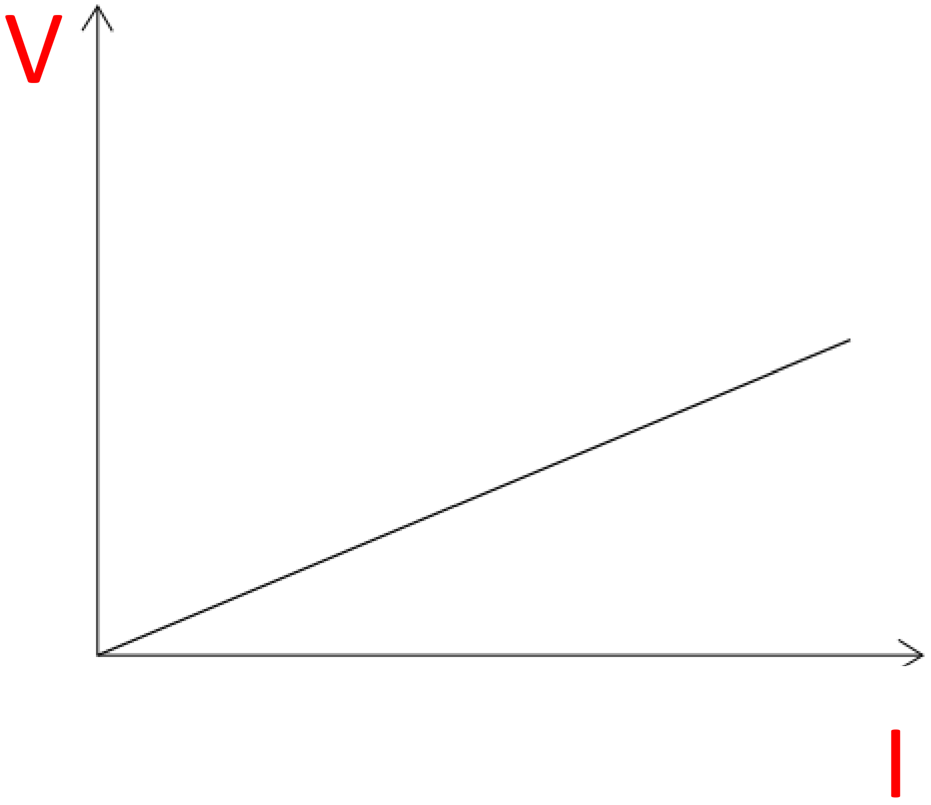
$$J = nev_d$$

n=free electron density
v_d = drift velocity

Come si misura la legge di Ohm?

V/I=R





$$R = \frac{V}{I}; \qquad R = \rho\frac{l}{S};$$

$$\rho = \frac{R \cdot S}{l};$$

resistività

LA CONDUZIONE ELETTRICA NEI METALLI

Introduzione

La struttura cristallina di un solido risulta dalla ripetizione regolare di ragguppamenti di atomi, che formano una cella elementare. Quando si applica un campo elettrico ad un solido metallico gli elettroni vengono accelerati e si muovono nel cristallo sotto l'influsso di una energia potenziale, dovuta alla carica positiva dei nuclei, schermata dagli elettroni localizzati sugli stessi atomi. Se gli atomi fossero molto distanti tra loro, le superfici di energia potenziale non si influenzerebbero tra di loro ed ogni atomo si potrebbe considerare un sistema isolato. Il calcolo dell'energia potenziale si ridurrebbe a quello di un sistema idrogenoide con carica Z ed effetto di schermo da parte degli elettroni più interni. In un ristallo reale l'energia potenziale è invece una funzione periodica, con periodicità pari alla cella elementare; l'elettrone si muove quindi sotto l'influenza di un campo periodico non nullo all'interno del reticolo, mentre dall'esterno viene sollecitato da un campo elettrico applicato (differenza di potenziale).

L'effetto del reticolo è sostanzialmente quello di introdurre una 'perturbazione periodica' alle caratteristiche del movimento dell'elettrone sotto l'influsso del campo elettrico. Questo fatto, diversamente da quanto spesso si suppone, non rallenta il moto elettronico e non introduce effetti di 'resistenza ohmica': in un reticolo idealmente perfetto ed in assenza di agitazione termica il moto dell'elettrone non incontrerebbe resistenza alcuna.

Come verrà approfondito più oltre, il comportamento dell'elettrone in potenziale periodico può venire descritto dalla meccanica ondulatoria come se l'elettrone subisse una trasformazione della sua massa in massa efficace, m^*. In questo modo può verire applicata al moto dell'elettrone l'equazione classica

$F = m^* \cdot a$. La massa efficace è abbastanza simile a quella reale per un conduttore metallico, mentre può discostarsi da questa in maniera significativa nei semiconduttori e diventare in alcuni casi anche 'formalmente' negativa.

La conduzione secondo un semplice modello

Si può supporre che verosimilmente la densità di corrente 'J ' sia proporzionale al campo elettrico applicato E secondo una costante 'σ ' detta conduttività elettrica (il suo reciproco 'ρ ' viene detto resistività elettrica):

$$J = E / \rho = \sigma \cdot E \quad \text{(legge di Ohm).}$$

La densità di corrente J viene definita come la quantità di carica che passa nell'unità di tempo attraverso l'unità di superficie. Il campo E viene misurato in Volt/metro. La legge di Ohm viene spesso scritta come $V = I \cdot R$ che fornisce la caduta di tensione attraverso una resistenza elettrica R quando fluisce la corrente elettrica totale I.

I metalli ad elevato grado di purezza sono i migliori conduttori elettrici, come in genere anche di calore. Un elettrone in movimento viene costantemente accelerato finchè non incontra sul suo cammino un difetto reticolare, una impurezza od un fonone (quanto di vibrazione reticolare), fattori che provocano tutti una deviazione dalla perfetta periodicità del reticolo metallico. Si genera in questo caso una interferenza tra il moto ondulatorio dell'elettrone e il difetto reticolare che provoca un trasferimento di quantità di moto dall'elettrone al reticolo, con l'effetto complessivo di diminuire la velocità dell'elettrone, di deviarlo dalla sua traiettoria e di aumentare l'energia cinetica degli atomi (con conseguente aumento di temperatura del solido).

Consideriamo il movimento di un singolo elettrone e di estenderlo poi al movimento complessivo degli elettroni collettivi sotto l'influsso del campo elettrico esterno. Supponiamo che l'elettrone possa muoversi ed accelerare liberamente fino all'istante della interazione con un difetto reticolare, un impurezza o un fonone, quando cede tutta la sua energia cinetica al reticolo. L'accelerazione dell'elettrone è data da $a = q \cdot E/m_e$, se il tempo medio tra due urti è 2τ (τ è detto tempo di rilassamento, per il Cu è stimato $2 \cdot 10^{-14}$ s) , la velocità dell'elettrone dopo 2τ, supposto che sia partito da $v = 0$, risulta $2\tau \cdot a = 2\tau \cdot q \cdot E/m_e$. Mediamente la sua velocità è da considerarsi a metà di questo processo, al tempo τ (come in figura),

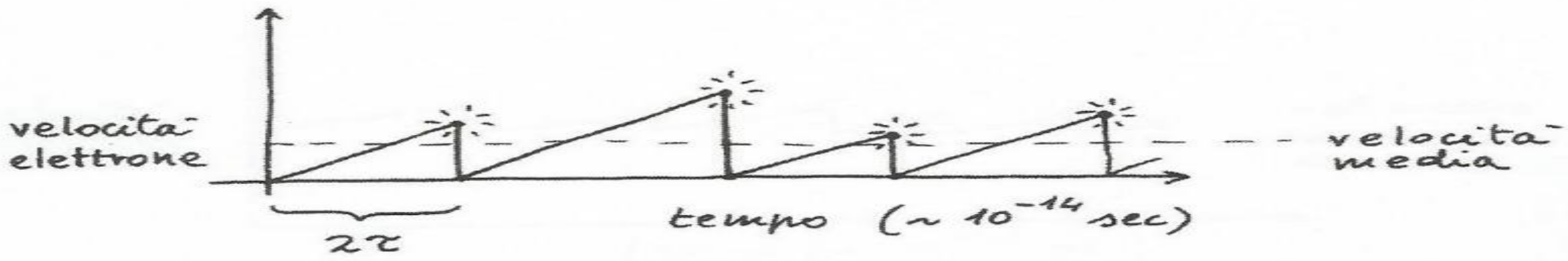


Fig. Velocità dell'elettrone in un metallo in funzione del tempo

per cui la velocità media dell'elettrone $v_{(media)}$ per tempi molto maggiori di τ (o velocità di deriva o drift) sarà data da :

$$v_{(media)} = (\tau \cdot q \cdot E)/m_e$$

Se la densità degli elettroni liberi è 'n ', la densità di corrente sarà data da :

$$J = n \cdot q \cdot v_{(media)} = (n \cdot q^2 \cdot E \cdot \tau) / m_e$$

e sostitendo nell'espressione della legge di Ohm si ottiene :

$$\sigma = (n \cdot q^2 \cdot \tau) / m_e$$

Occorre a questo punto introdurre il concetto, abbastanza intuitivo, di mobilità dell'elettrone, o in generale di un portatore di carica (nei semiconduttori i portatori di carica possono essere lacune), indicato come $\mu-$ (o $\mu+$ per una lacuna). Questa mobilità viene definita come il rapporto tra la velocità media (o di deriva) del portatore e l'intensità del campo elettrico:

$$\mu- = \frac{v_{(media)}}{E} = \frac{q \cdot \tau}{m_e}$$

Ne deriva che la conducibilità σ sarà anche data da

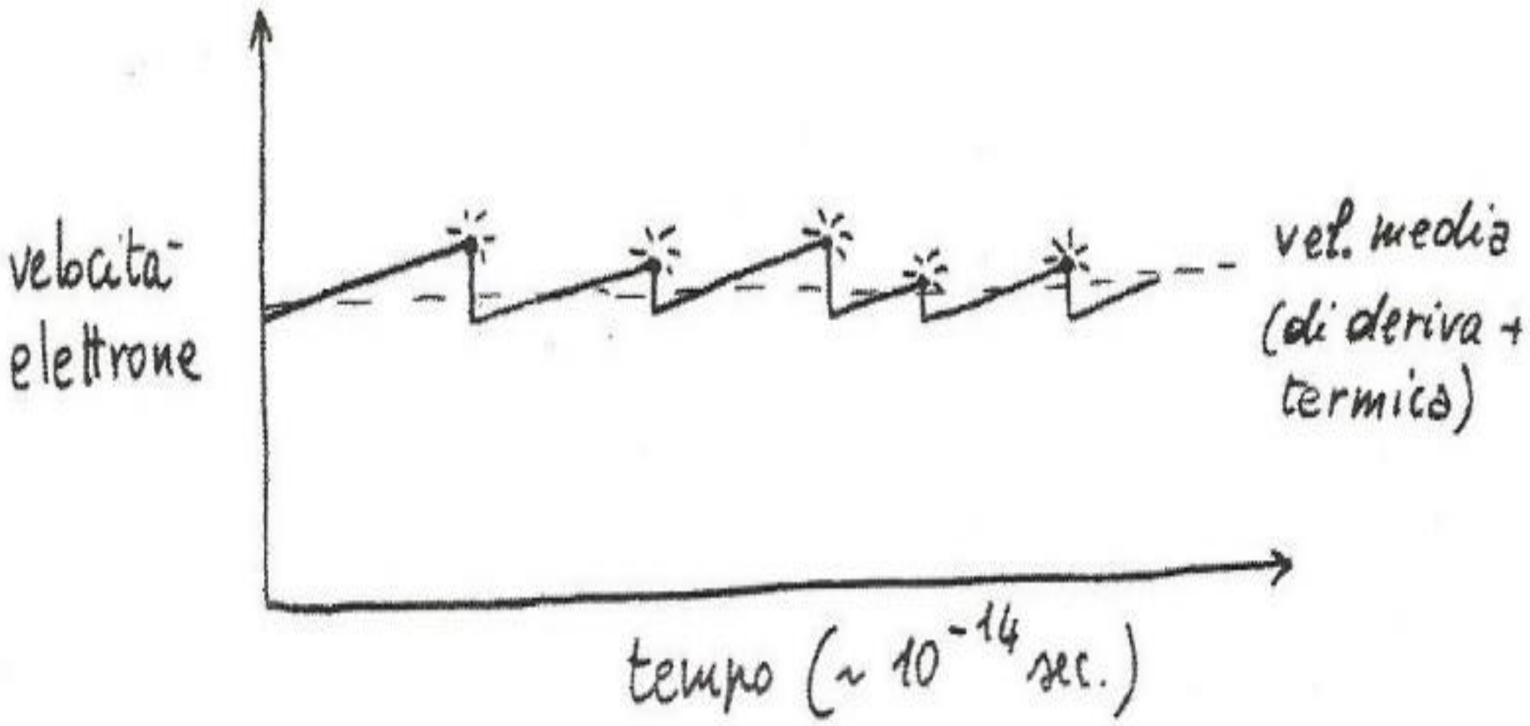
$$\sigma = (n \cdot q^2 \cdot \tau)/m_e = n \cdot q \cdot \mu+$$

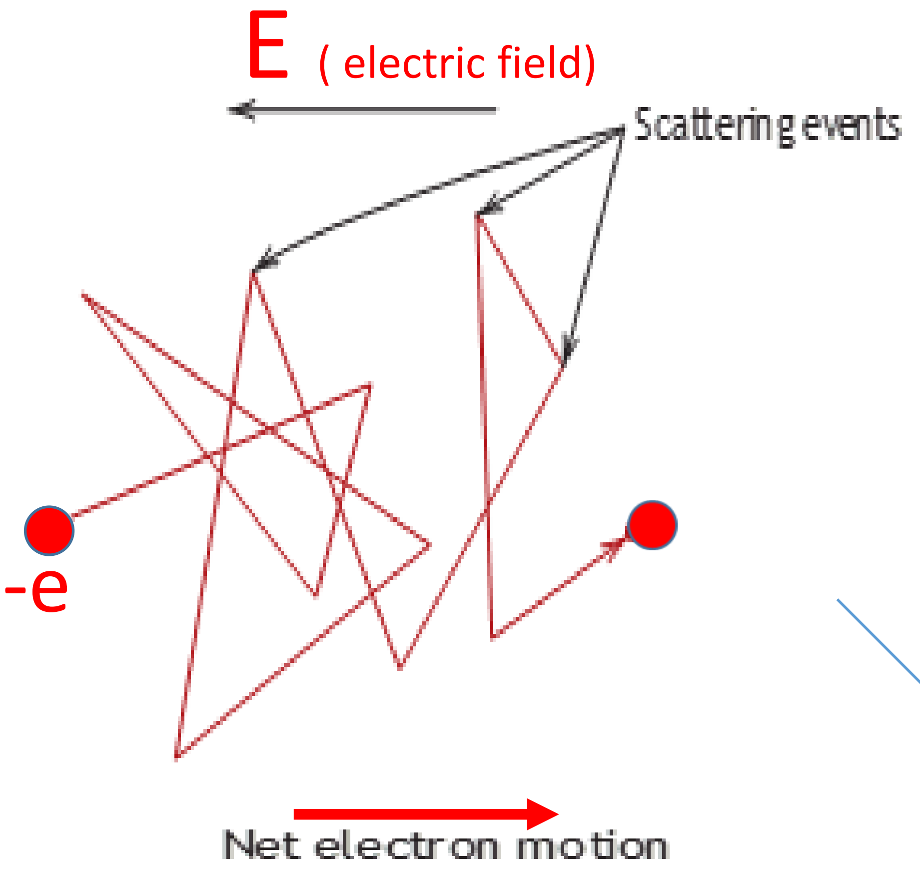
relazione valida anche se i portatori sono lacune ($\mu+$ viene sostituito da $\mu-$).

La velocità degli elettroni, anche in questo semplice modello, non può essere soltanto dovuta al campo elettrico esterno. Bisogna considerare il contributo termico, additivo a quello di deriva dovuto al trasferimento di energia cinetica durante le 'collisioni' con il reticolo per cui la velocità totale risulta :

$$V_{tot} = V_{term} + V_{deriva}$$

La componente termica è costante tra le collisioni mentre la componente di deriva aumenta tra esse. Possiamo quindi disegnare uno schema più realistico, pur con i limiti di questo modello semplificato,





Velocità dell'elettrone in funzione del tempo secondo un modello più realistico

Una stima della componente termica della velocità si può avere immaginando che gli elettroni si comportino come gli atomi di un gas perfetto, sostituendo agli urti tra atomi le collisioni con il reticolo. La statistica di Maxwell governa la distribuzione delle energie cinetiche in un gas e quindi la velocità delle particelle. In particolare la velocità media secondo questa statistica risulta eguale a :

$$v_{(media)} = \sqrt{(8 \cdot k_B \cdot T)/m_e)}$$

Gli ordini di grandezza di $v_{(media)}$ e v_{term} sono notevolmente lontani. Facciamo un semplice calcolo per il rame metallico. Per questo metallo σ vale $5{,}81 \cdot 10^{-7} \cdot \Omega^{-1} m^{-1}$ ed n, numero dei portatori, può essere considerato eguale al numero di atomi (vedasi la configurazione elettronica del rame con un unico elettrone nella sfera di valenza 4s) per cui si ha $n = 1{,}16 \cdot 10^{29}\ m^{-3}$ e quindi $\tau = 1{,}79 \cdot 10^{-14}$s. Supponendo un campo elettrico di 0,32 V/m per semplificare i calcoli si ha quindi

$$v_{(media)} = 1 \cdot 10^{-3}\ m/s \qquad v_{term} = 1{,}1 \cdot 10^{5}\ m/s$$

Di conseguenza, salvo campi elevatissimi, $v_{(media)} \approx 10^{-8} \cdot v_{term}$.

Ne risulta che, anche senza campo applicato gli elettroni di conduzione si muovono in modo disordinato molto rapidamente, con velocità dell'ordine di 10^6 m/s ; poiché il loro movimento avviene in ogni direzione non risulta alcun flusso netto di corrente.

Nella realtà questo modello semplificato, detto talvolta a 'palle da biliardo' risulta del tutto inadeguato, infatti l'applicazione di un campo elettrico accelera solamente alcuni degli elettroni in direzione del campo provocando un flusso netto di cariche. Soltanto una parte degli elettroni può subire infatti una variazione di energia (provocata dalla accelerazione); per un elettrone molto al di sotto del livello di Fermi infatti tutti gli stati adiacenti sono pieni e quindi non sono accessibili per il principio di esclusione di Pauli. Solo se gli viene fornita una quantità abbastanza grande di energia, tale da spingerlo al di sopra del livello di Fermi esso può accelerare, ma considerando che l'energia dei quanti di vibrazione reticolare (fononi) in un solido raggiunge qualche centesimo di eV, tale processo è improbabile ; quindi non può esservi accelerazione graduale a meno che l'elettrone non si trovi al di sopra od appena sotto il livello di Fermi.

Si può dimostrare che l'elettrone può trovare livelli liberi solo se la sua energia è superiore a $(E_F - kT)$; la densità 'n' degli elettroni liberi alla temperatura ambiente risulta così circa l'1 per cento della densità degli elettroni risiedenti nella banda di conduzione.

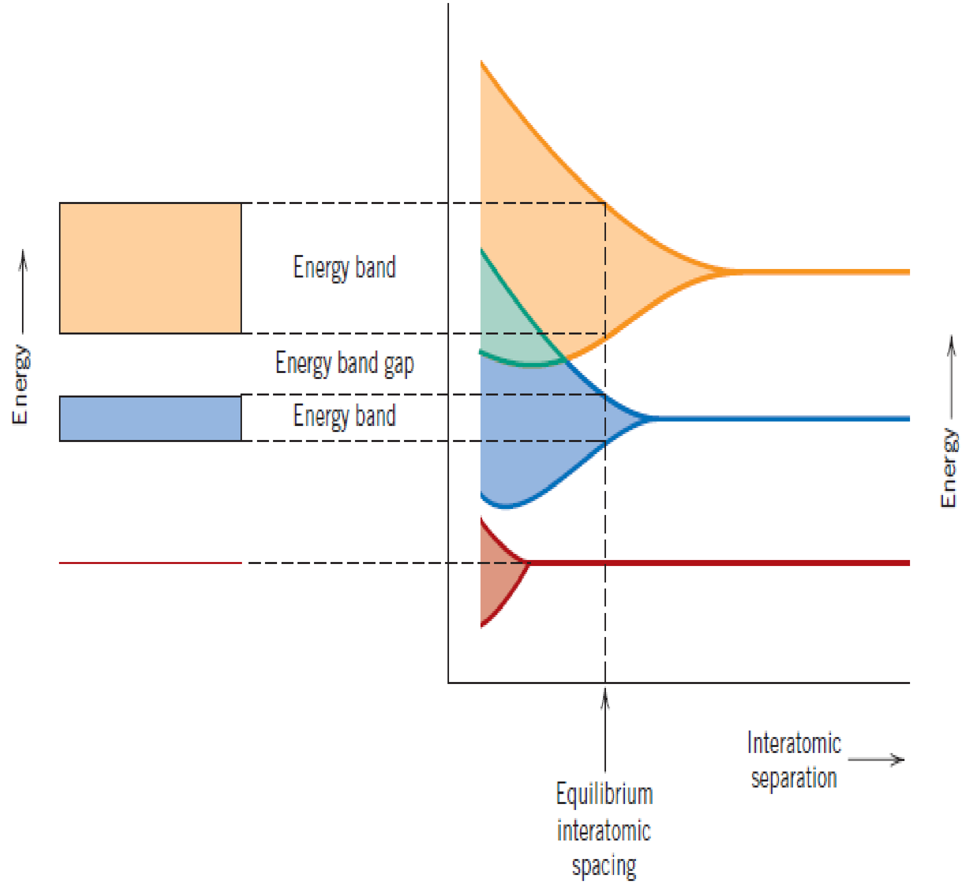
La velocità media v definita nel paragrafo precedente diventa quindi una velocità di deriva (drift, v_d) degli elettroni della banda di valenza, considerando anche quelli 'congelati' per il principio di esclusione. Non vengono presi in considerazione i movimenti casuali degli elettroni, anche se elevati, perchè essendo completamente casuali non portano in realtà contributo netto alla conduzione. Per il rame si stimano così velocità di drift di 4,4 cm/s in un conduttore di lunghezza pari a 1 metro e con 10 Volt applicati agli estremi supponendo che ogni atomo di Cu contribuisca con un elettrone alla conduzione. In realtà la velocità di quegli elettroni che contribuiscono in un certo istante alla conduzione è molto maggiore in quanto essi sono in realtà molto minori in numero.

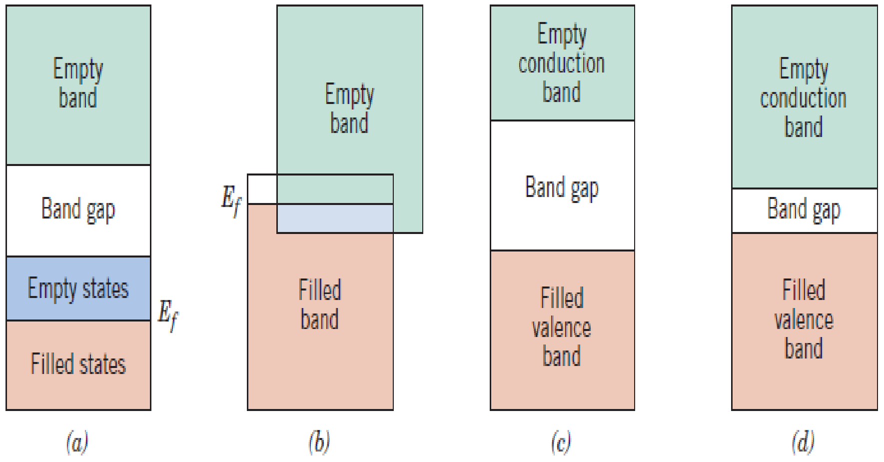
Conduzione elettrica e struttura a bande

Nei metalli la combinazione degli orbitali atomici dà luogo ad una serie anche piuttosto complessa di bande, le cui energie possono anche sovrapporsi in parte. Ad esempio la combinazione di N orbitali 2s produce una banda che può ospitare 2N elettroni o la combinazione dei livelli 2p produce una banda p che può ospitare 6N elettroni. La banda più alta, se è solo parzialmente piena e contiene il livello di Fermi è detta banda di conduzione perché solo gli elettroni vicini a questo livello possono condurre. Nei metalli la banda di conduzione è di norma solo parzialmente piena; nel rame, per esempio, gli elettroni di valenza 4s riempiono solo metà della banda s più esterna, poiché c'è soltanto un elettrone 4s per ogni Cu (come si deduce dalla sua configurazione elettronica).

In alcuni metalli la banda di valenza piena si sovrappone con una banda più alta parzialmente vuota e gli elettroni di tali metalli sono ancora in grado di muoversi perché la banda extra fornisce degli stati vuoti.

Supponiamo che la banda di valenza sia completamente piena e che la banda più alta successiva sia completamente vuota e non sia possibile alcuna sovrapposizione di bande. Nessun elettrone può rispondere ad un campo elettrico esterno aumentando la sua velocità (e anche la sua energia) a meno ché non possa raggiungere uno degli stati vuoti nella banda più alta. Per fare questo un elettrone deve attraversare l'intervallo di energia proibito tra le bande; anche se tale intervallo risulta di qualche elettronVolt, occorrono dei campi elettrici molto elevati per portare gli elettroni nella banda più elevata (supponendo che il libero cammino medio tra gli 'urti' sia di 50 nm, si può calcolare che sono necessari campi di 10^8 V/m o maggiori). In questa situazione, senza elettroni liberi il materiale si comporta come un isolante. Se l'intervallo di energia diminuisce al di sotto di 2 eV l'effetto della temperatura sulla distribuzione di Fermi-Dirac può essere tale che alcuni elettroni passano nella banda di conduzione. Tali materiali vengono detti semiconduttori.





Legge di Ohm (1870) $V = RI$

R indipendente da I e da V
mentre dipende dalla geometria del conduttore
ρ (resistività)

$E = \rho J \qquad J = \dfrac{I}{A}$ → sezione del filo

$V = EL$ ← lunghezza del conduttore

$$V = EL = \rho J L = \rho \frac{I}{A} L = \frac{\rho L}{A} I \Longrightarrow R = \rho \frac{L}{A}$$

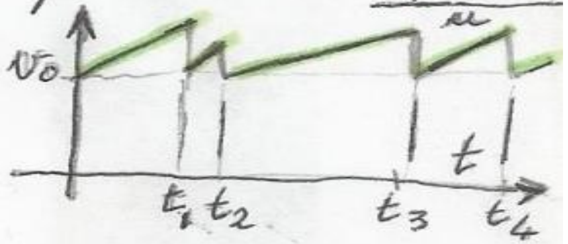
Siano n gli elettroni per unità di volume, in un tempo dt avanzano di $v\,dt$, $n(v\,dt)A$ sia il numero di elettroni che attraversano l'area A, la carica che attraversa l'area A è $\underbrace{-e \cdot n(v\,dt)A}$ $\Longrightarrow$ $J = -n e v_{deriva}$

La velocità media in funzione del campo è $\overline{v}_{deriva}(t) = -\frac{e}{m} E t$

velocità acquistata nel tempo t

$v_{tot}(t) = v_0 + \overline{v}_{deriva}(t)$ v_0 velocità termica

$\tau = \frac{t_1 + t_2 + \ldots t_n}{n}$



$\overline{v}_{deriva} = -\frac{eE}{m}\tau$ $J = \left(\frac{n e^2 \tau}{m}\right) E = \sigma E$

σ conducibilità elettrica $= +\frac{n e^2 \tau}{m}$ $\tau = \frac{m}{n e^2 \rho}$

modello di Drude (1900)

τ	77 °K ($\times 10^{-14}$ sec)	273 °K	373 °K
Li	7.3	0.9	0.6
Cu	3.1	2.7	1.9
Pb	0.57	0.14	0.09

$l = v_F \tau$ (l cammino libero medio) classicamente $\frac{1}{2} m v^2 = \frac{3}{2} K T$

sperimentalmente $l \sim 10^2 \div 10^3$ Å $l \sim 10$ Å $v \sim 10^7$ cm/sec

Microscopic View of Copper Wire

As an example of the microscopic view of Ohm's law, the parameters for copper will be examined. With one free electron per atom in its metallic state, the electron density of copper can be calculated from its bulk density and its atomic mass.

$$n = \frac{(6.02x10^{23} atoms/mole)(8.92x10^{3} kg/m^{3})}{63.5x10^{-3} kg/mole} = 8.46x10^{28}/m^{3}$$

The Fermi energy for copper is about 7 eV, so the Fermi speed is

$$v_F = c\sqrt{\frac{2E_F}{mc^2}} = 3x10^{8} m/s\sqrt{\frac{2x7eV}{511000eV}} = 1.57x10^{6} m/s$$

The measured conductivity of copper at 20°C is

$$\sigma = 5.9x10^{7}/\Omega m$$

The mean free path of an electron in copper under these conditions can be calculated from

$$d = \frac{\sigma m v_F}{ne^2} = \frac{(5.9x10^{7}/\Omega m)(9.11x10^{-31} kg)(1.57x10^{6} m/s)}{(8.46x10^{28}/m^{3})(1.6x10^{-19})^2} = 3.9x10^{-8} m$$

The drift speed depends upon the electric field applied. For example, a copper wire of diameter 1mm and length 1 meter which has one volt applied to it yields the following results.

$$R = \frac{L}{\sigma A} = \frac{1m}{(5.9x10^{7}/\Omega m)(\pi .0005^{2} m^{2})} = 0.0216\Omega$$

For 1 volt applied this gives a current of 46.3 Amperes and a current density

$$J = 5.9x10^{7} A/m^{2}$$

This corresponds to a drift speed of only millimeters per second, in contrast to the high Fermi speed of the electrons.

$$v_d = \frac{J}{ne} = \frac{5.9x10^{7} A/m^{2}}{(8.46x10^{28}/m^{3})(1.6x10^{-19} C)} = 0.0043 m/s$$

Room-Temperature Electrical Conductivities for Nine Common Metals and Alloys, Electrical Conductivity (’Ω.m)$^{-1}$

Metal	
Silver	6.8 x 10^7
Copper	6.0 x 10^7
Gold	4.3 x 10^7
Aluminum	3.8 x 10^7
Brass (70Cu–30Zn)	1.6 x 10^7
Iron	1.0 x 10^7
Platinum	0.9 x 10^7
Plain carbon steel	0.6 x 10^7
Stainless steel	0.2 x 10^7

Electrical conductivity

sigma= n x e^2 x tau /m*

m* = massa efficace

OPTICAL PROPERTIES OF Matter and Materials

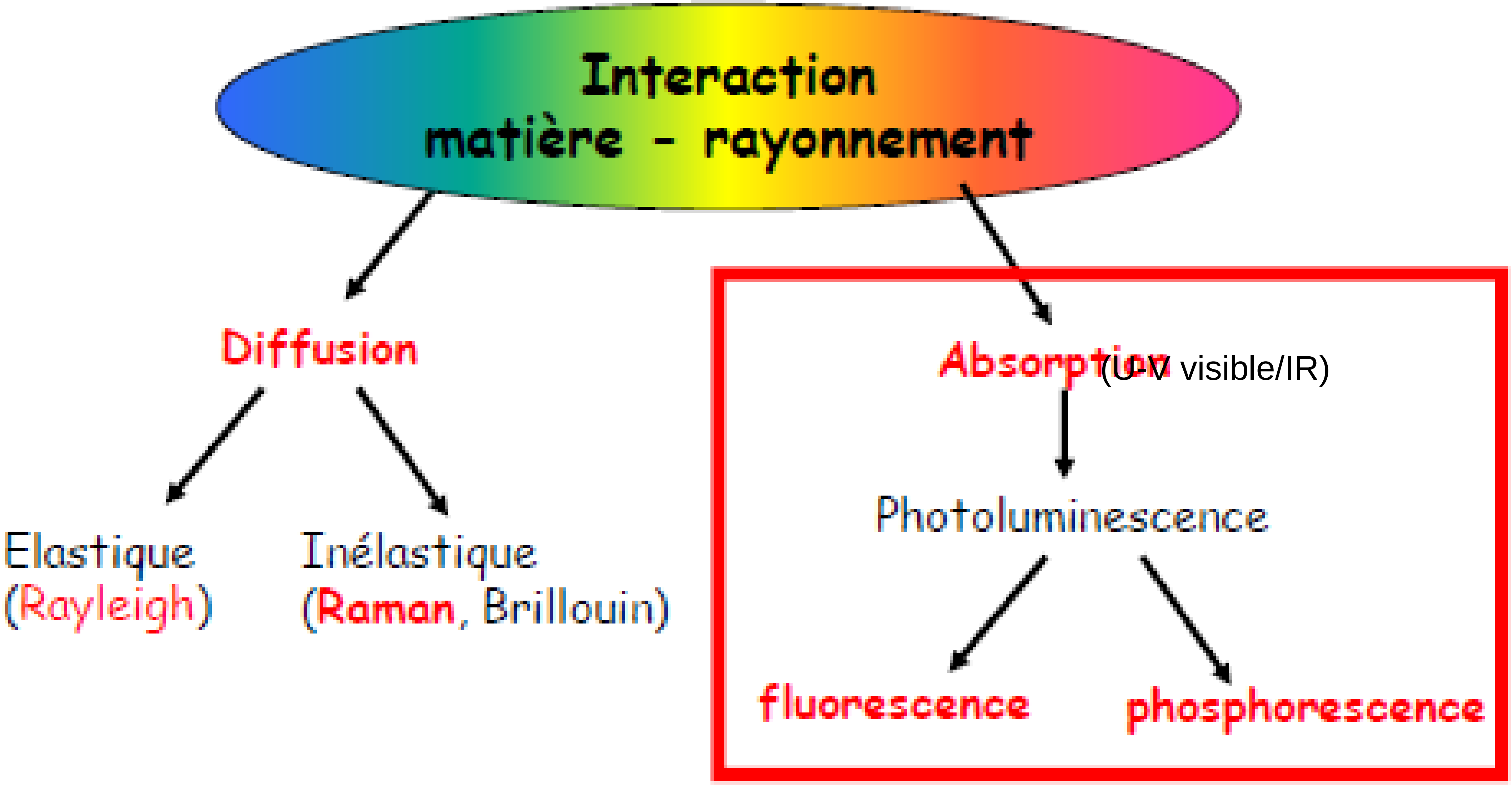
Material: Any solid fabricated and shaped by man for its use and its development

Material : Solid + Properties + Behavior laws

Spectroscopy: any experimental method in which the matter (the solid) will exchange energy with the outside environment, most of the time by an interaction with particles or radiation (in particular light)

Optical and vibrational Spectroscopies : the radiation is on the visible or infrared range

→ Electromagnetic waves in the appropriate range of energy



Interaction matière - rayonnement

Diffusion

Elastique (Rayleigh)

Inélastique (**Raman**, Brillouin)

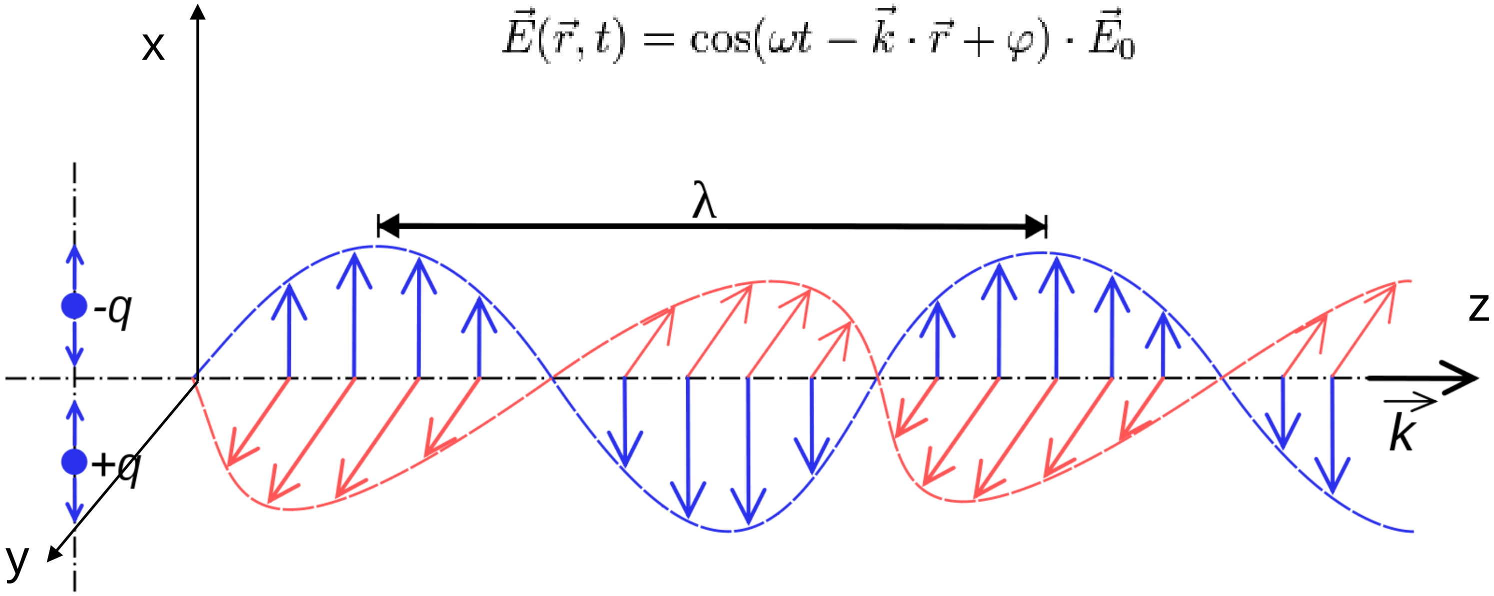
Absorption (U-V visible/IR)

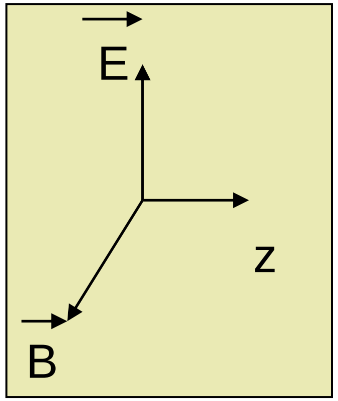
Photoluminescence

fluorescence

phosphorescence

$$\vec{E}(\vec{r},t) = \cos(\omega t - \vec{k}\cdot\vec{r} + \varphi)\cdot\vec{E}_0$$





A monochromatic electromagnetic wave can be modelled by a vibrating electrostatic dipole. The variations of the electric and magnetic fields are monitored by the Maxwell equations , then the wave can be represented par only one of these fields, in general the electric field. We can then write the general equation of a monochromatic plane wave:

$$\vec{E}(z,t) = \cos\omega(t - \frac{z}{c}) \qquad \vec{E}(z,t) = \cos(\omega t - \frac{2\pi}{T}\frac{z}{c}) = \cos(\omega t - \frac{2\pi}{\lambda}z)$$

$$\vec{E}\,(z,t) = \cos(\omega t - k_z z) \qquad \text{or} \qquad \vec{E}\,(z,t) = \mathrm{Re}\, e^{i(\omega t - k_z z)}$$

In which ω is the pulsation and its value 2πc/λ

Electromagnetic waves (EM waves):

$E = h\ \nu$	Energy with $h = 6{,}626$ J.s and ν (frequency) expressed in Hz ou s^{-1} h = Planck constant
$\lambda = c / \nu$	Wavelength with $c = 2{,}998 \ . \ 10^{8}$ m/s (light velocity in vacuum) λ expressed either in Å, en nm ou en μm
$\sigma = 1/\lambda = \nu/c$	Wavenumber, inverse of a length expressed in cm^{-1}, in particular in IR spectroscopy, also in Raman scattering
$\omega = 2\pi\nu$	pulsation associated to the EM wave (rad/s)
E	Energy expressed in Joules in the SI, but often in eV

Correspondances:

1 eV corresponds to: $1{,}602\ 10^{-19}$ J
$2{,}418\ 10^{14}$ Hz
8065 cm^{-1}
11600 K

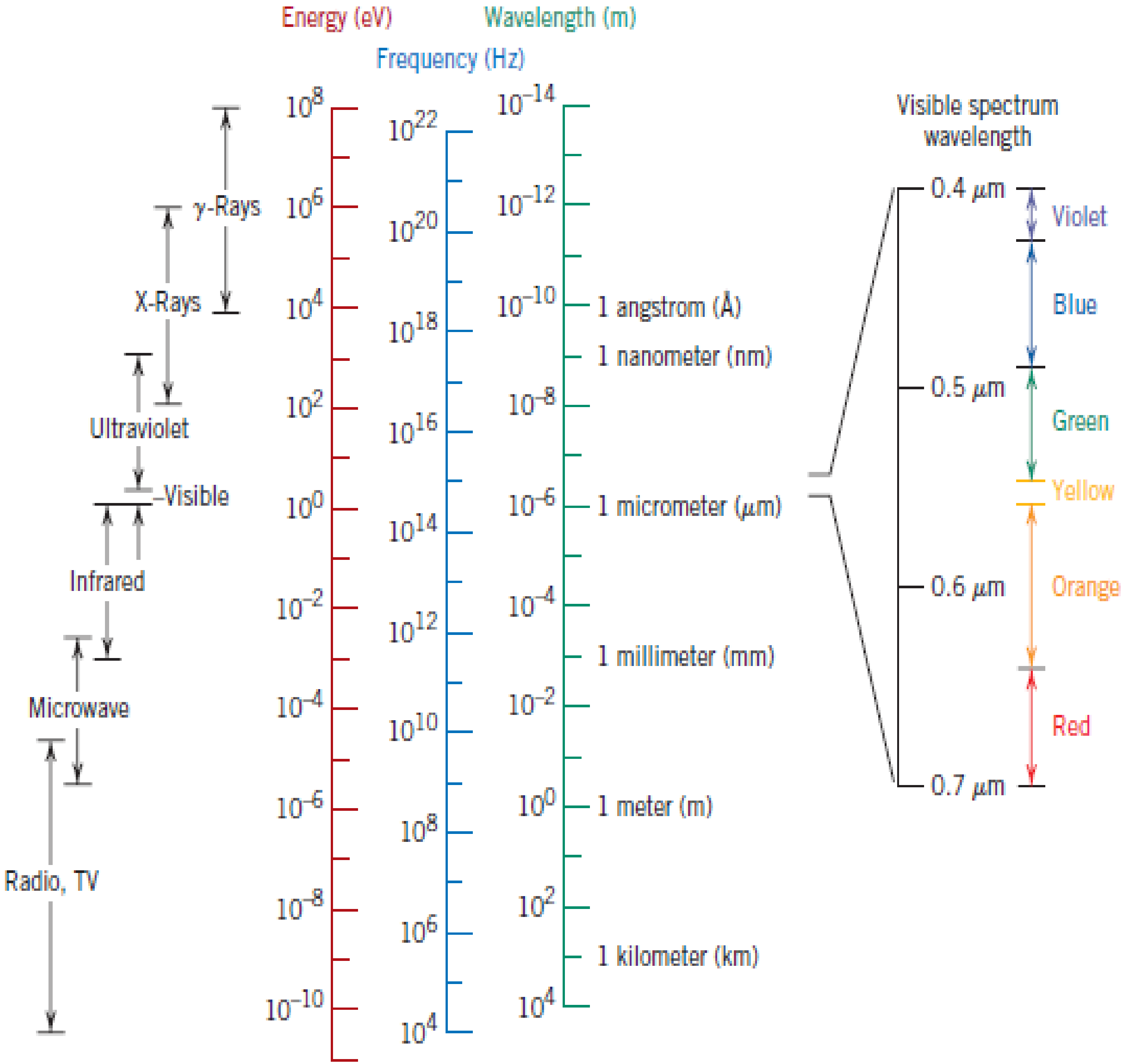
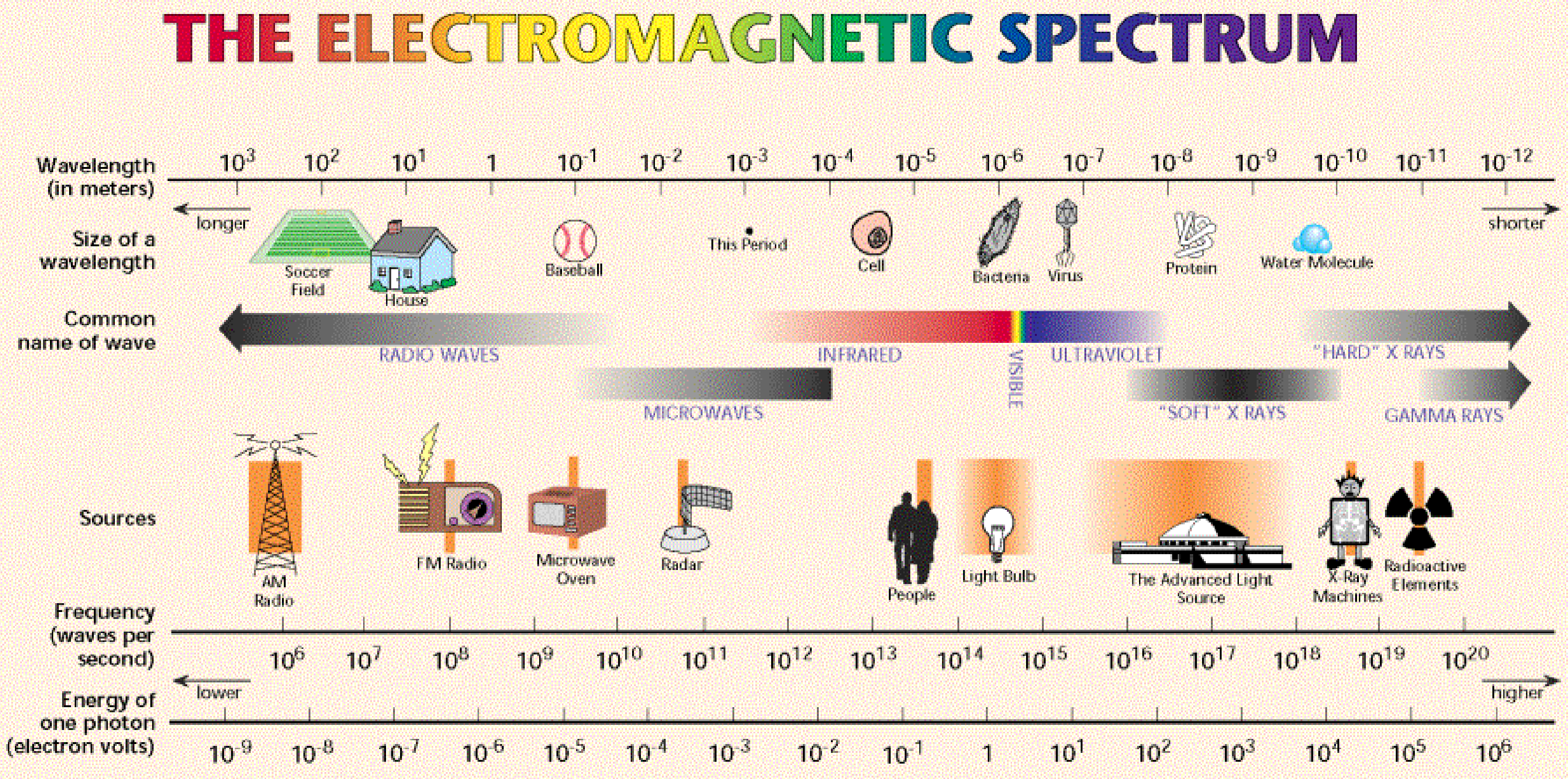


Figure 21.2 The spectrum of electromagnetic radiation, including wavelength ranges for the various colors in the visible spectrum.



Correspondence between wavelengths, frequencies and energies for photons
In the electromagnetic spectrum

jc.fs/emspectrum/9-96

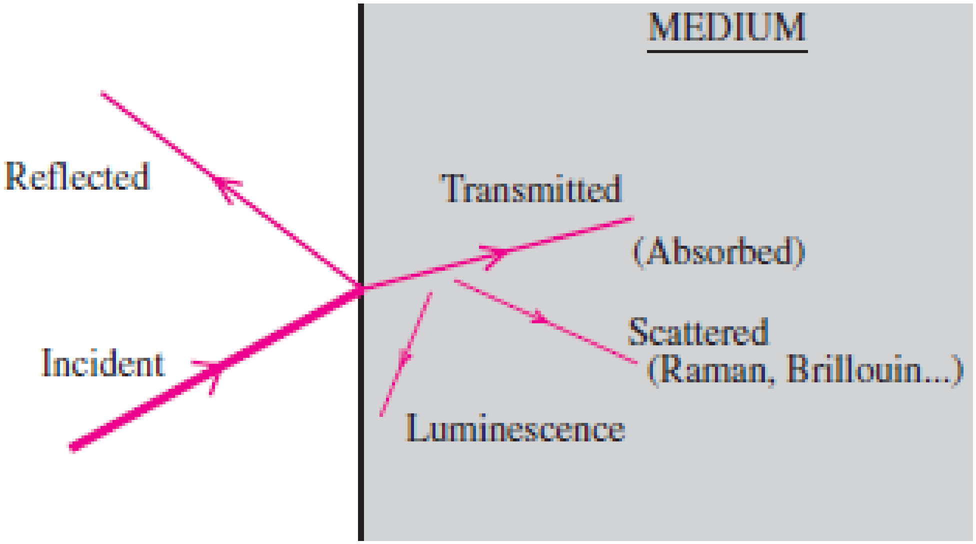
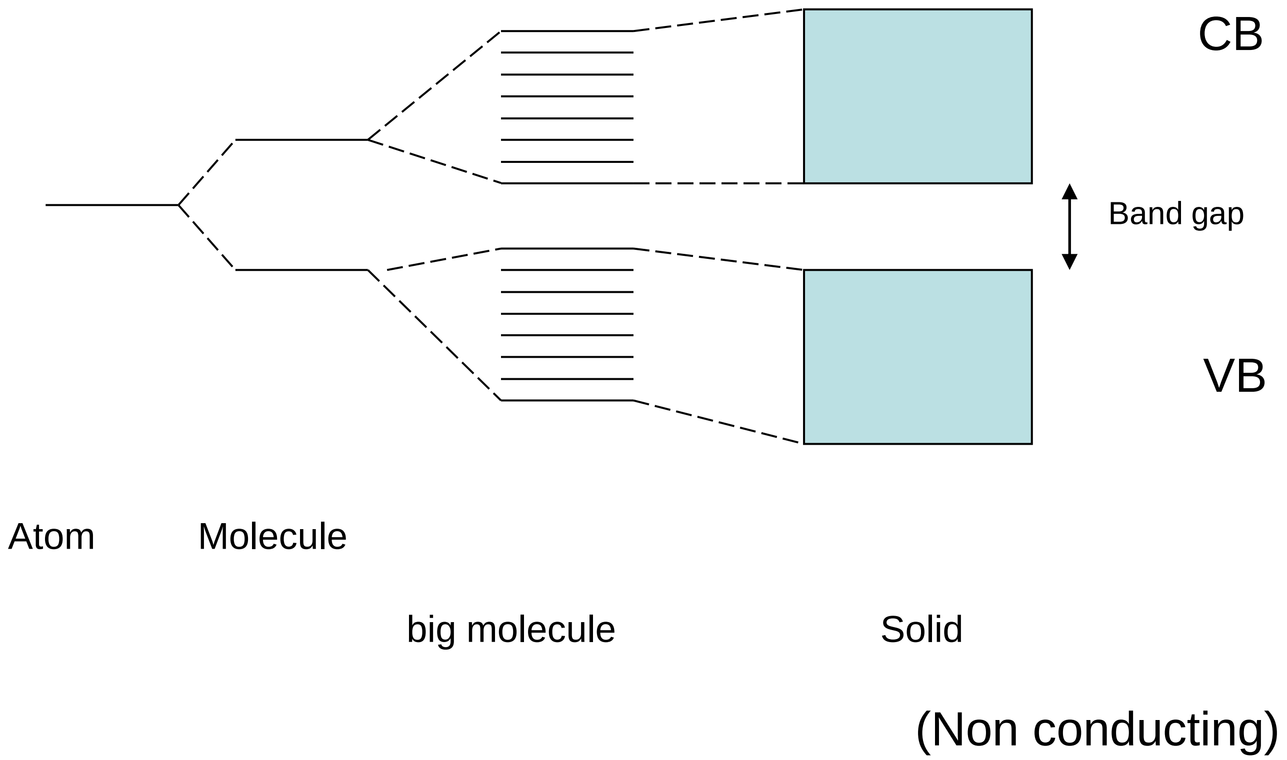


Fig. 6.1. Schematic diagram showing the linear optical processes that occur at the surface and in the interior of a medium. The incident beam is assumed to arrive at the surface of the medium from vacuum (or air)

The response of a medium to a light beam will strongly depend upon the nature and the structure of the material. We will for exemple make a distinction between:

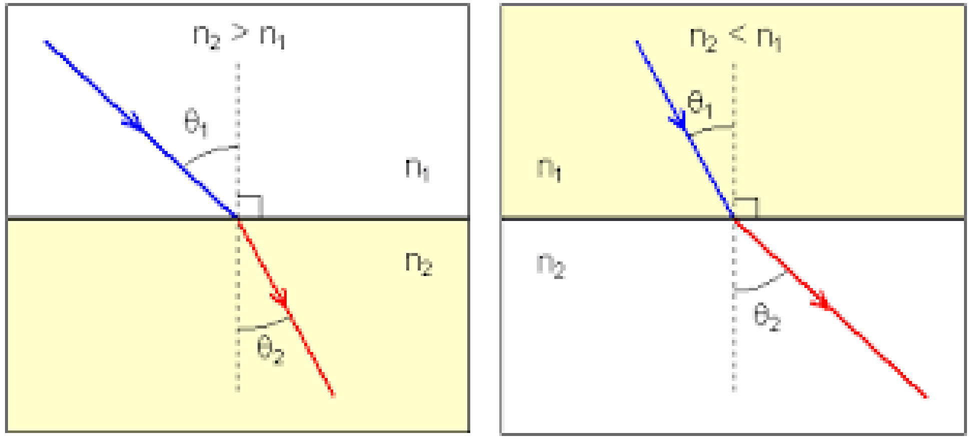
- A molecule/ a compact material
- The electronic nature of the material, i.e. insulating, semiconducting, conducting
- The amorphous or cristalline state of the material



Energy diagram for different systems

Optical constants

- Index of refraction : n
- known from the Snell - Descartes laws
- $n_1 \sin \theta_1 = n_2 \sin \theta_2$ $n = \sin \theta_1 / \sin \theta_2$
- $n = c/v$
- c: velocity of light in vacuum, v in medium



- Damping constant : k

$$c^2 \frac{\partial^2 \mathscr{E}_x}{\partial z^2} = \varepsilon \frac{\partial^2 \mathscr{E}_x}{\partial t^2} + 4\pi\sigma \frac{\partial \mathscr{E}_x}{\partial t},$$

$$\mathscr{E}_x = \mathscr{E}_0 \exp\left[i\omega\left(t - \frac{zn}{c}\right)\right],$$

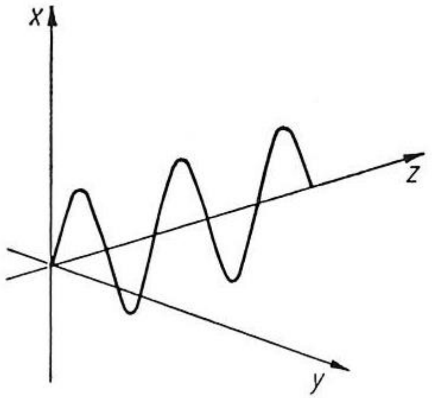


Figure 10.1. Plane polarized wave which propagates in the positive *z*-direction and vibrates in the *x*-direction.

In general, n is a complex entity

$$\hat{n}^2 = \varepsilon - \frac{4\pi\sigma}{\omega} i = \varepsilon - \frac{2\sigma}{\nu} i.$$

$$\hat{n} = n_1 - in_2.$$

$$\hat{n} = n - ik.$$

$$\hat{n}^2 = n^2 - k^2 - 2nik = \varepsilon - \frac{2\sigma}{\nu} i.$$

$$\varepsilon = n^2 - k^2,$$

$$\sigma = nk\nu.$$

k : damping constant

$$\varepsilon_1 = n^2 - k^2$$

$$\hat{n}^2 = n^2 - k^2 - 2nik \equiv \hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2.$$

$$\varepsilon_2 = 2nk = \frac{2\sigma}{\nu}.$$

$$n^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{2\sigma}{\nu}\right)^2} + \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1),$$

$$k^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{2\sigma}{\nu}\right)^2} - \varepsilon\right) = \frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1).$$

ε_2 represents the absorption
For insulators, k=0 and $\varepsilon_1 = n^2$

We define a **characteristic penetration depth**, W, as that distance at which the intensity of the light wave, which travels through a material, has decreased to $1/e$ or 37% of its original value, i.e., when

$$\frac{I}{I_0} = \frac{1}{e} = e^{-1}. \tag{10.20}$$

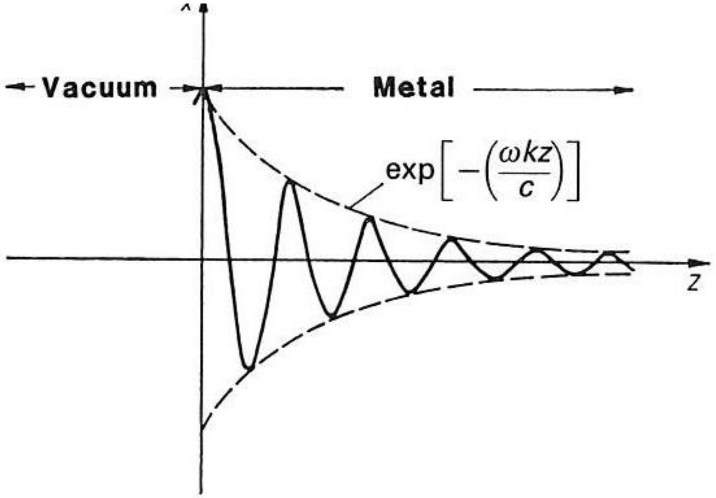
Table 10.1. Characteristic Penetration Depth, W, and Damping Constant, k, for Some Materials ($\lambda = 589.3$ nm).

Material	Water	Flint glass	Graphite	Gold
W(cm)	32	29	6×10^{-6}	1.5×10^{-6}
k	1.4×10^{-7}	1.5×10^{-7}	0.8	3.2

We return now to (10.5) in which we replace the index of refraction by the complex index of refraction (10.8). This yields

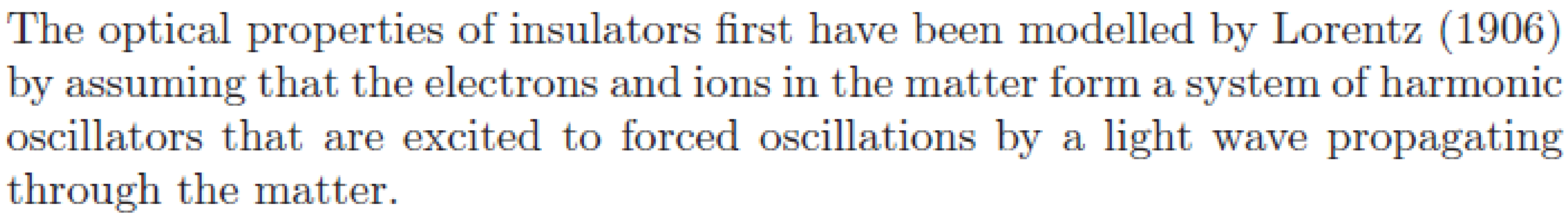
$$\mathcal{E}_x = \mathcal{E}_0 \exp\left[i\omega\left(t - \frac{z(n-ik)}{c}\right)\right], \tag{10.17}$$

$$\boxed{\mathcal{E}_x = \underbrace{\mathcal{E}_0 \exp\left[-\frac{\omega k}{c} z\right]}_{\text{Damped amplitude}} \cdot \underbrace{\exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]}_{\text{Undamped wave}} .}$$

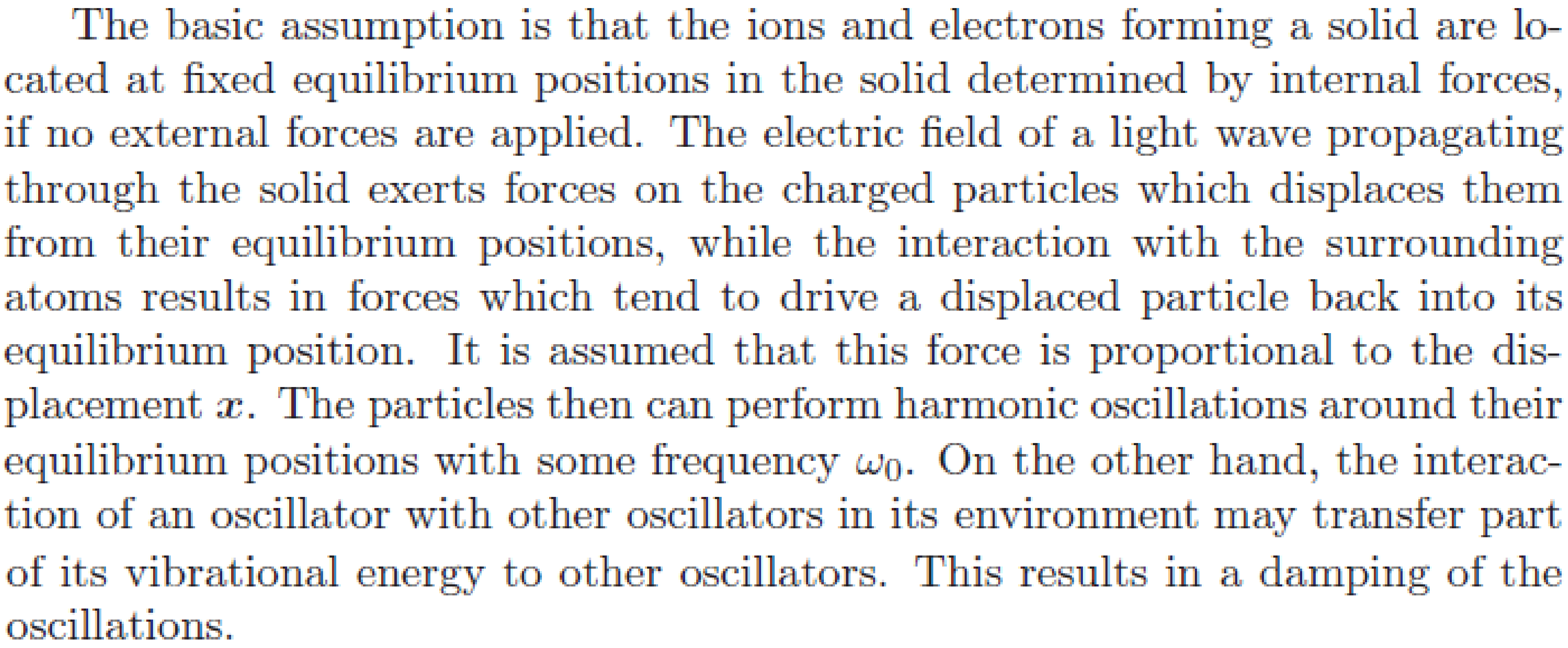


Modulated light wave. The amplitude decreases exponentially.

Lorentz model for insulators



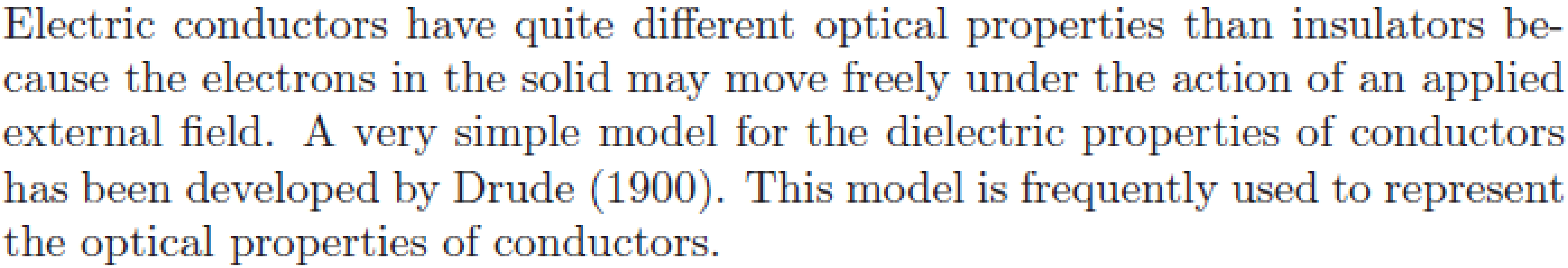
The optical properties of insulators first have been modelled by Lorentz (1906) by assuming that the electrons and ions in the matter form a system of harmonic oscillators that are excited to forced oscillations by a light wave propagating through the matter.



The basic assumption is that the ions and electrons forming a solid are located at fixed equilibrium positions in the solid determined by internal forces, if no external forces are applied. The electric field of a light wave propagating through the solid exerts forces on the charged particles which displaces them from their equilibrium positions, while the interaction with the surrounding atoms results in forces which tend to drive a displaced particle back into its equilibrium position. It is assumed that this force is proportional to the displacement x. The particles then can perform harmonic oscillations around their equilibrium positions with some frequency ω_0. On the other hand, the interaction of an oscillator with other oscillators in its environment may transfer part of its vibrational energy to other oscillators. This results in a damping of the oscillations.

Equation of motion $$m\ddot{x} + m\gamma\dot{x} + m\omega_0^2 x = - eE_{\text{loc}} \, .$$

Drude model for conductors (1900)



Electric conductors have quite different optical properties than insulators because the electrons in the solid may move freely under the action of an applied external field. A very simple model for the dielectric properties of conductors has been developed by Drude (1900). This model is frequently used to represent the optical properties of conductors.

Maxwell equations

Maxwell equations describe how electric and magnetic fileds are generated and altered by each other and by charges and currents

In the MKSA system:

$$\nabla . \boldsymbol{E} = \frac{\rho}{\epsilon_0} \qquad = 0 \text{ if no charges}$$

$$\nabla . \boldsymbol{B} = 0$$

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

$$\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j} + \epsilon_0 \mu_0 \frac{\partial \boldsymbol{E}}{\partial t}$$

In the CGS system:

$$\nabla . \boldsymbol{E} = 0$$

$$\nabla . \boldsymbol{H} = 0$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}$$

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

Reminder:
J = **σ E,** σ conductivity
D = ε E, dielectric constant
J electrical current
D electrical displacement

$$\vec{\nabla}(\vec{u}) = \vec{\nabla} \bullet \vec{u} = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}$$

$$\nabla \times \nabla \times \nabla = \nabla.(\nabla.\boldsymbol{E}) - \nabla^2 \boldsymbol{E}$$ Mathematical identity

$$= - \nabla^2 \boldsymbol{E}$$ Since $\nabla.\boldsymbol{E} = 0$

$$-\nabla^2 \boldsymbol{E} = -\frac{1}{c}\frac{\partial}{\partial t}(\nabla \times \boldsymbol{H})$$

$$= -\frac{1}{c}\frac{\partial}{\partial t}\left(\frac{4\pi}{c}\boldsymbol{j} + \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t}\right)$$

$$= \frac{\omega^2}{c^2}\left(1 + \frac{4\pi i \sigma}{\omega}\right)\boldsymbol{E}$$

since $j = \sigma \boldsymbol{E}$ and $\boldsymbol{E} = \boldsymbol{E_0} e^{i(\boldsymbol{k}.\boldsymbol{r} - \omega t)}$

$$\boxed{\tilde{\varepsilon}(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}}$$

$$-\nabla^2 \boldsymbol{E}(\omega) = \frac{\omega^2}{c^2}\,\tilde{\varepsilon}(\omega)\,\boldsymbol{E}(\omega)$$

with

$$\tilde{\varepsilon}(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}$$

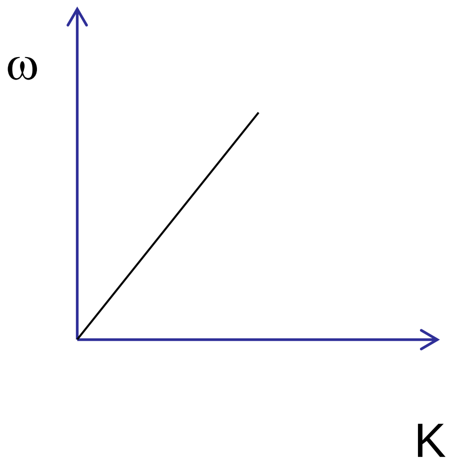
Dielectric function

$$\boldsymbol{E}(\omega) = \boldsymbol{E}_0\, e^{i(Kx-\omega t)}$$

For a propagation in the x direction

$$\Longrightarrow \qquad \omega = \frac{cK}{\sqrt{\tilde{\varepsilon}(\omega)}}$$

Relationship for the dispersion of the wave



$$\epsilon(\omega,\mathbf{K})\,\omega^2 = c^2K^2$$

Different models are then established, depending on the type of materials
The value of ε is of primary importance

Let take first a metal: considered as a gas of electrons.
Let look at the response of the dielectric function at long wavelengths, i.e. for K=0

$$m\frac{d^2x}{dt^2}=-eE\ .$$

Equation of motion of a free electron in an electric field

If x and E have the time dependence $e^{-i\omega t}$, then

$$-\omega^2 mx=-eE\ ;\qquad x=eE/m\omega^2\ .$$

$$P=-nex=-\frac{ne^2}{m\omega^2}E\ ,$$

Polarization: dipole moment per unit volume, n is the electron concentration

$$\epsilon(\omega)\equiv\frac{D(\omega)}{E(\omega)}\equiv 1+4\pi\frac{P(\omega)}{E(\omega)}\qquad\qquad \epsilon(\omega)=1-\frac{4\pi ne^2}{m\omega^2}$$

We define the plasma* frequency as:

$$\omega_p{}^2\equiv 4\pi ne^2/m\ ;$$

$$\boxed{\epsilon(\omega)=1-\frac{\omega_p{}^2}{\omega^2}\ ,}$$

* A plasma is a medium with an equal concentration of positive and negative charges

If the positive ion background has a dielectric constant labeled $\epsilon(\infty)$ essentially constant up to frequencies well above ω_p, then (8) becomes

$$\epsilon(\omega) = \epsilon(\infty) - 4\pi ne^2/m\omega^2 = \epsilon(\infty)[1 - \tilde{\omega}_p{}^2/\omega^2] \ , \tag{11}$$

where $\tilde{\omega}_p$ is defined as

$$\tilde{\omega}_p{}^2 = 4\pi ne^2/\epsilon(\infty)m \ . \tag{12}$$

Notice that $\epsilon = 0$ at $\omega = \tilde{\omega}_p$.

Dispersion Relation for Electromagnetic Waves

$$\epsilon(\omega,\mathbf{K})\omega^2 = c^2K^2$$

$$\boxed{\epsilon(\omega) = 1 - \frac{{\omega_p}^2}{\omega^2} \ ,}$$

This relation tells us a great deal. Consider

1. $\epsilon > 0$. For ω real, K is real and a transverse electromagnetic wave propagates with the phase velocity $c/\epsilon^{\frac{1}{2}}$.
2. $\epsilon < 0$. For ω real, K is imaginary and the wave is damped with a characteristic length $1/|K|$.
3. $\epsilon = \infty$. This means the system has a finite response in the absence of an applied force; thus the poles of $\epsilon(\omega,\mathbf{K})$ define the frequencies of the free oscillations of the medium.
4. $\epsilon = 0$. We shall see that longitudinally polarized waves are possible only at the zeros of ϵ.
5. ϵ complex. For ω real, $\mathbf{K}$ is complex at the zeros and poles of ϵ, and the waves are damped in space.

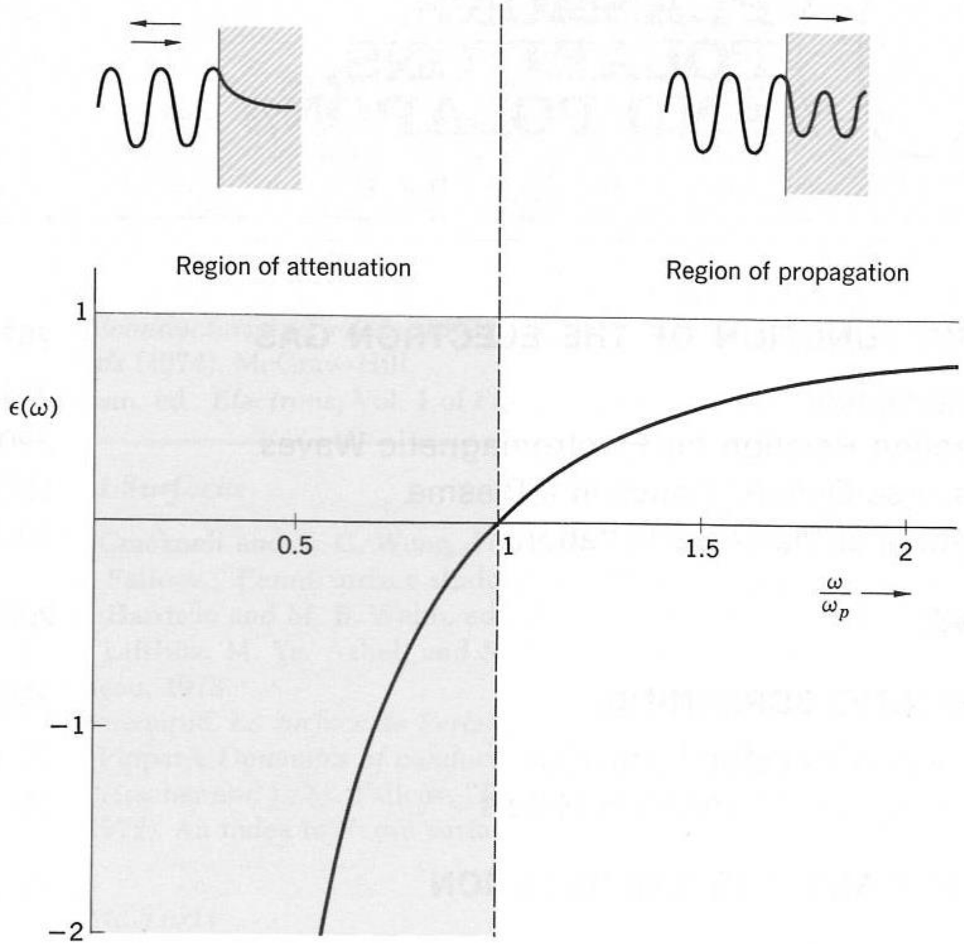


Figure 1 Dielectric function $\epsilon(\omega)$ of a free electron gas versus frequency in units of the plasma frequency ω_p. Electromagnetic waves propagate only when ϵ is positive. Electromagnetic waves are totally reflected from the medium when ϵ is negative.

1. *Assumptions of the Drude model*

The Drude model is based on the following assumptions:

- The metal has a density n mobile carriers, where n is a number/cm^3 (number density, not mass density).
- These carriers are typically electrons,* with charge $q = -e$.
- The carriers are free. This statement means that the internal restoring force is zero, or the potential is constant.
- The carriers do not interact; the electron-electron potential is neglected.
- If set in motion, the carriers relax to equilibrium do to a damping from collisions. This damping is taken as a frictional or viscous force, proportional to the drift velocity of the carriers.†
- Apply Newton's laws to an electron whose coordinate is at $\vec{r}$.

$$\sum \vec{F} = m\vec{a} = m\ddot{\vec{r}}$$

- The forces are $-e\vec{E}$ and $\Gamma\vec{v} = -\Gamma\dot{\vec{r}}$.
- Linear response, so coordinates, velocities, accelerations have the same time dependence as the field $\vec{E}$.
- The electric field is the applied field $\vec{E}_{\text{ext}}$ and not some local field because the electrons sample all parts of the crystal and average over the dipole fields of the atoms. See page 40 for more on this subject.

Considering only the time dependance

$$\boldsymbol{E} = \boldsymbol{E}_0 \, e^{i\omega t}$$

$$x = x_0 \, e^{i\omega t}$$

$$m \frac{d^2x}{dt^2} + m\,\Gamma \, \frac{dx}{dt} = -e\boldsymbol{E}$$

$$\longrightarrow \qquad x = \frac{eE}{m\,(\omega^2 + i\omega\Gamma)}$$

$$\epsilon = \frac{D}{E} = 1 + 4\pi \, \frac{P}{E} \qquad\qquad P = -nex$$

$$\epsilon = 1 - \frac{4\pi n e^2}{m} \times \frac{1}{\omega^2 + i\,\omega\Gamma}$$

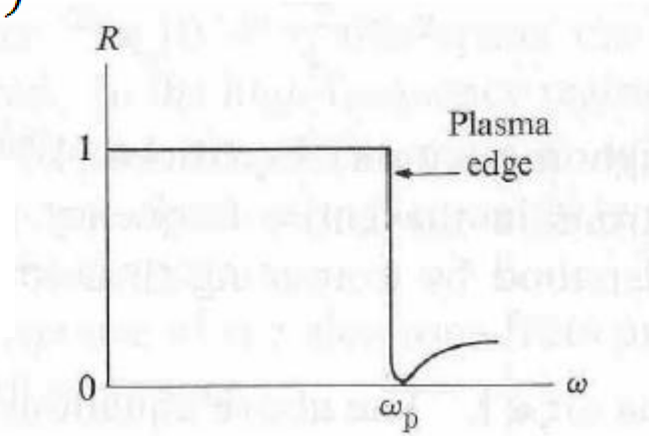
$$\boxed{\epsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}}$$

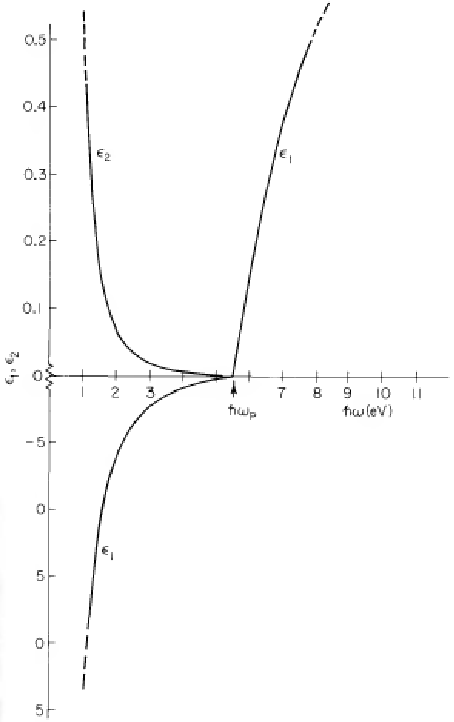
$$\epsilon = \epsilon_1 + i\epsilon_2$$

$$\epsilon_1 = 1 - \frac{\omega_p^2}{(\omega^2 + \Gamma^2)}$$

$$\epsilon_2 = \frac{\omega_p \Gamma}{\omega(\omega^2 + \Gamma^2)}$$

$$R = \left|\frac{1-N}{1+N}\right|^2 = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2},$$





pendence of ε_1 and ε_2 for a free-electron metal. The calculations are for $Ne^2/m = \omega_p^2 = 30$ eV^2 and $\hbar\Gamma = 0.02$ eV. Note the difference in scale the positive and negative axes. The magnitude of ε_1 is much greater than ency range shown. For $\hbar\omega < \hbar\Gamma$, $|\varepsilon_2/\varepsilon_1| \to \Gamma/\omega$ and ε_2 dominates.

We can see from Eq.(20) that the high-frequency region can now be divided into two subregions: In the subregion $\omega < \omega_p$, $\varepsilon < 0$, and consequently, from (7), $n = 0$. In view of (8), this leads to $R = 1$. That is, the metal exhibits *perfect reflectivity*. In the higher subregion $\omega > \omega_p$,and $\varepsilon > 0$, and hence, by similar reasoning, $k = 0$. In this range, therefore, $\alpha = 0$, $0 < R < 1$, and the metallic medium acts like a nonabsorbing transparent dielectric, e.g., glass.

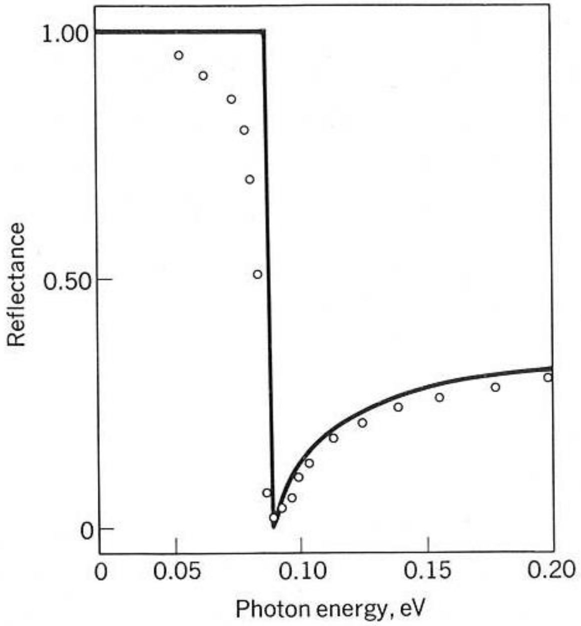


Figure 3 Reflectance of indium antimonide with $n = 4 \times 10^{18}\ \mathrm{cm}^{-3}$. [After W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957), from J. N. Hodgson.]

Table 1: Reflection Edges (Plasma Frequencies) and Corresponding Wavelengths for Some Metals

	Li	Na	K	Rb
ω_p ($10^{16}\mathrm{s}^{-1}$)	1.22	0.89	0.593	0.55
λ_p (Å)	1550	2100	3150	3400

TABLE 1 Ultraviolet Transmission Limits of Alkali Metals, in Å

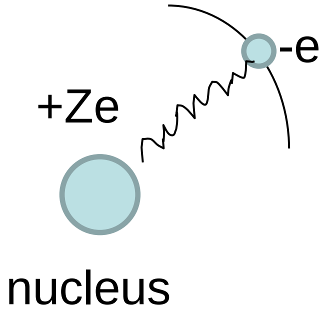
	Li	Na	K	Rb	Cs
λ_p, calculated, mass m	1550	2090	2870	3220	3620
λ_p, observed	1550	2100	3150	3400	–

LORENTZ MODEL FOR INSULATORS AND SEMICONDUCTORS

$$m\frac{d^2x}{dt^2} + m\,\Gamma\,\frac{dx}{dt} + m\,\omega_0^2 = \; -e\boldsymbol{E}$$

$$x = \frac{eE}{m\,(\omega^2 - \omega_0^2 \, + \, i\omega\Gamma)}$$

$$\epsilon = 1 - \frac{4\pi n e^2}{m} \times \frac{1}{\omega^2 - \omega_0^2 + \; i\,\omega\Gamma}$$



Contribution to the electronic polarisibility to the dielectric constant

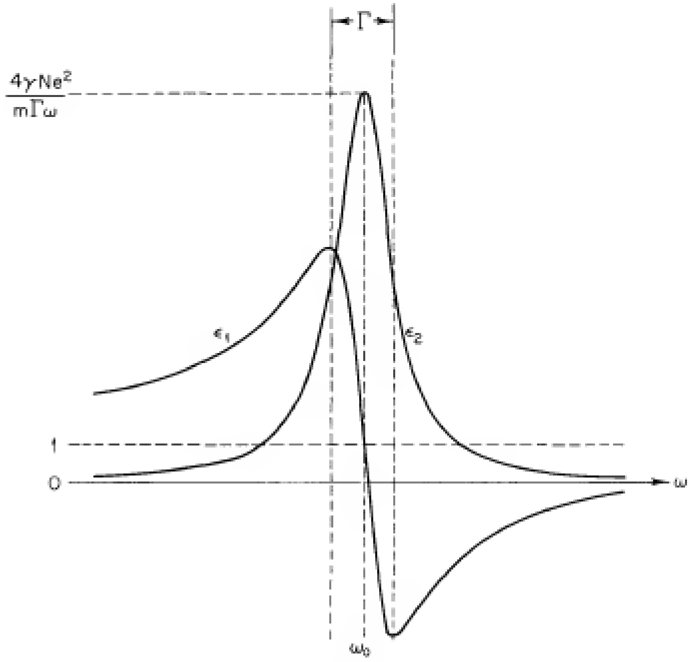


Fig. 3.1 Frequency dependence of ε_1 and ε_2.

Figure 3.1 shows that except for a narrow region near ω_0, ε_1 increases with increasing frequency. This is called normal dispersion. However, there is a region near ω_0 where ε_1 decreases with increasing frequency. This is called anomalous dispersion. We can find the width of the region of anomalous dispersion as follows. Equating the derivative of Eq. (3.14) to zero, we find

$$(\omega_0{}^2 - \omega_m{}^2)^2 = \pm\,\omega_0{}^2\Gamma^2 \tag{3.20}$$

where ω_m is the frequency at which ε_1 is a maximum or a minimum. If the region of anomalous dispersion is reasonably narrow, $\omega_m \approx \omega_0$,

$$(\omega_0 - \omega_m) = \pm\,\Gamma/2 \tag{3.21}$$

and the full width of the region of anomalous dispersion is Γ. In the absence of an energy loss mechanism, there is a singularity at ω_0.

If

$$\Gamma \approx 0 \tag{3.22}$$

ε_2 versus ω is a bell-shaped curve which is symmetric about ω_0. Small values of Γ compared with ω_0 cause little distortion. From Eq. (3.15), we find that the maximum value of ε_2 is

$$\varepsilon_2(\max) = \frac{4\pi Ne^2/m}{\Gamma\omega_0} \tag{3.23}$$

assuming the maximum occurs exactly at ω_0. Also, the full width of the ε_2 curve at half maximum is Γ.

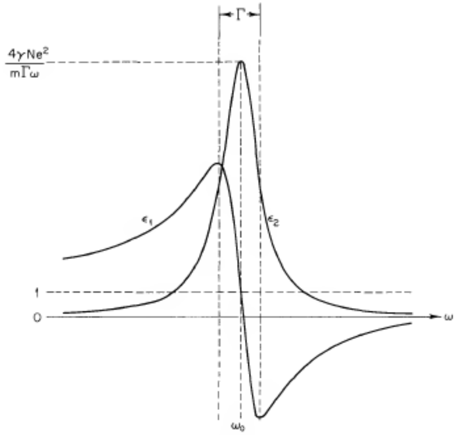


Fig. 3.1 Frequency dependence of ε_1 and ε_2.

Implications for the optical properties of solids

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

$$n = \{\tfrac{1}{2}[(\varepsilon_1{}^2 + \varepsilon_2{}^2)^{1/2} + \varepsilon_1]\}^{1/2}$$

$$k = \{\tfrac{1}{2}[(\varepsilon_1{}^2 + \varepsilon_2{}^2)^{1/2} - \varepsilon_1]\}^{1/2}$$

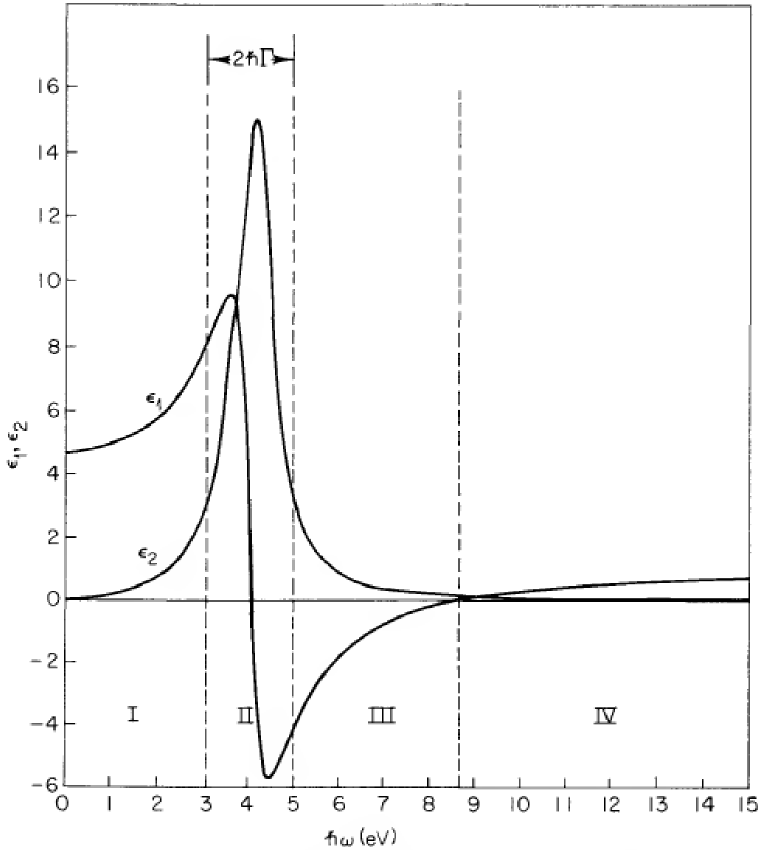


Fig. 3.3 Spectral dependence of ε_1 and ε_1. The curves are calculated for the case in $\hbar\omega_0 = 4$ eV, $\hbar\Gamma = 1$ eV, and $4\pi Ne^2/m = 60$. The onset of region IV is defined by $\varepsilon_1 = 0$.

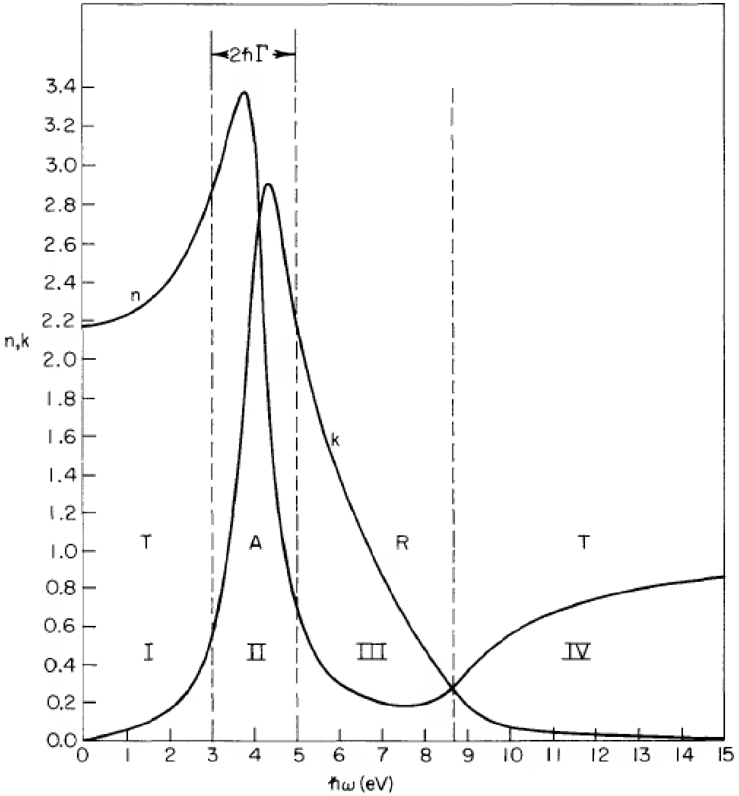


Fig. 3.4 Spectral dependence of *n* and *k*. The curves are calculated from the values of ε_1 and ε_2 given in Fig. 3.3. The regions I, II, III, and IV can be seen to be primarily transmitting (T), absorbing (A), reflecting (R), and transmitting (T), respectively. These results follow from consideration of Eq. (3.24) and the realization that strong absorption takes place only in the neighborhood of a transition frequency.

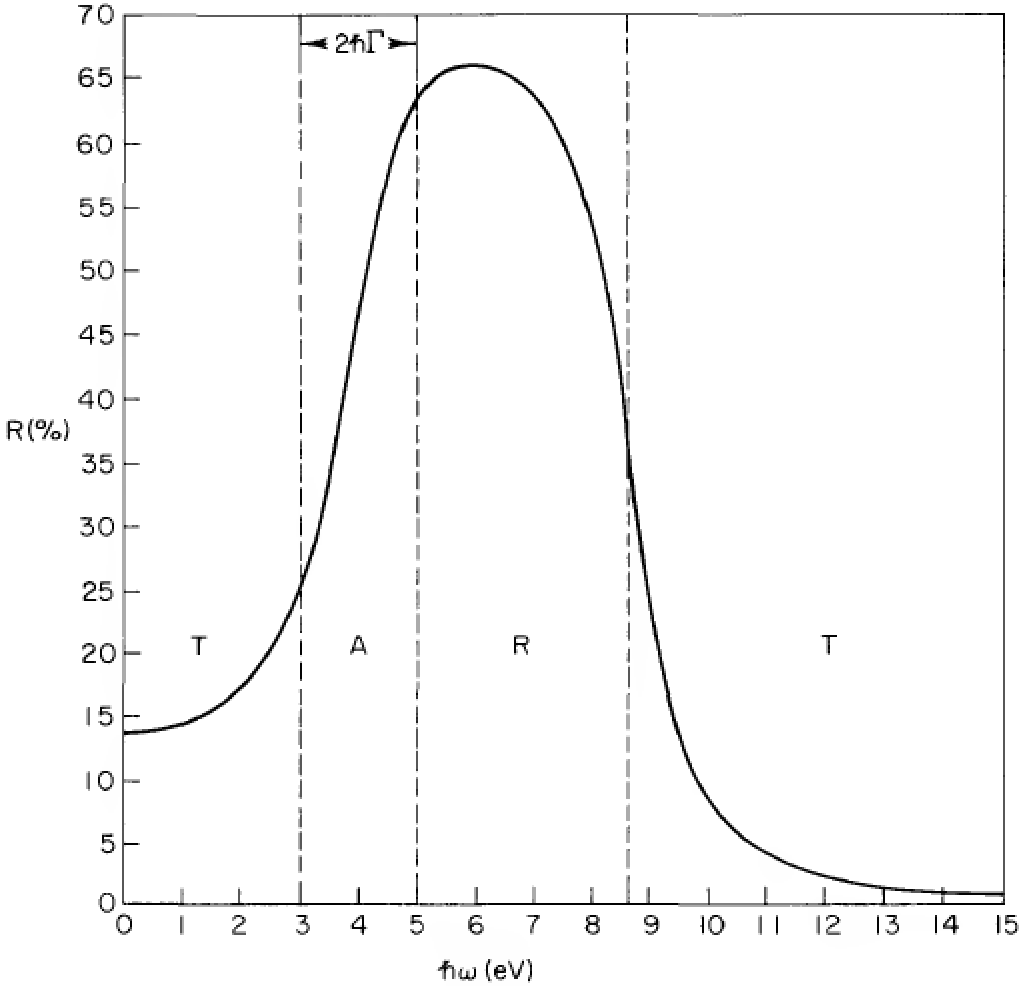
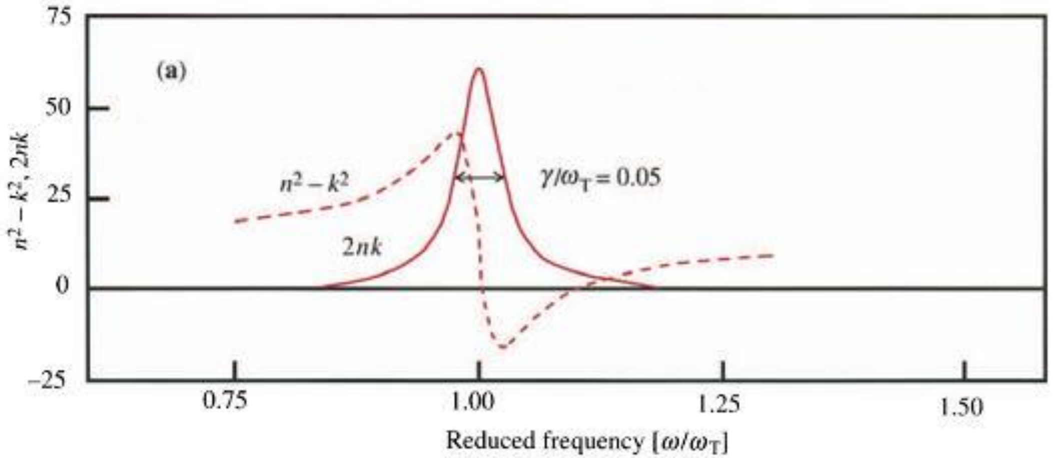
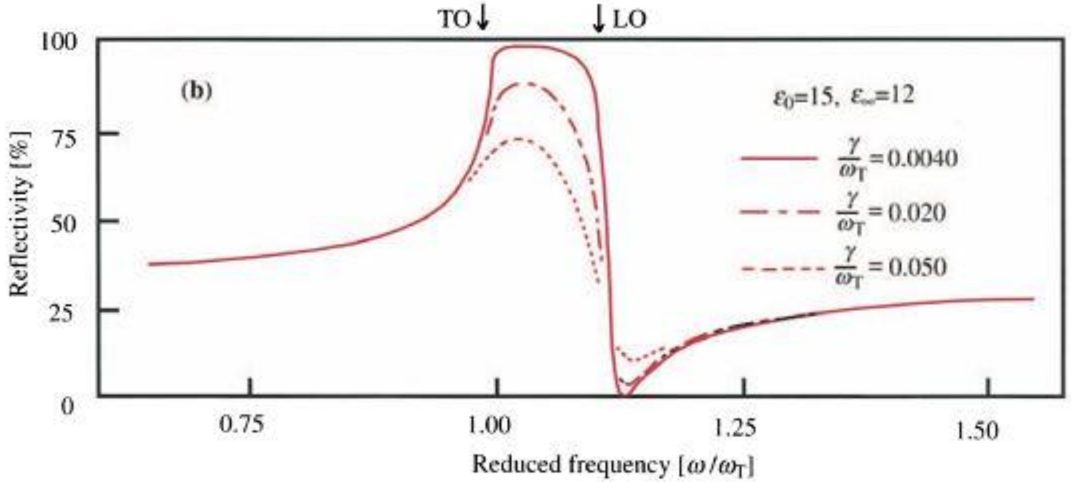


Fig. 3.5 Spectral dependence of reflectivity. The curve is calculated from the *n* and *k* values given in Fig. 3.4.



Real and imaginary part of the complex dielectric constant calculated for a Zinc blende structure



Reflectivity coefficients calculated from different values of the damping factor γ

Two arrows indicate LO and TO, phonon frequencies

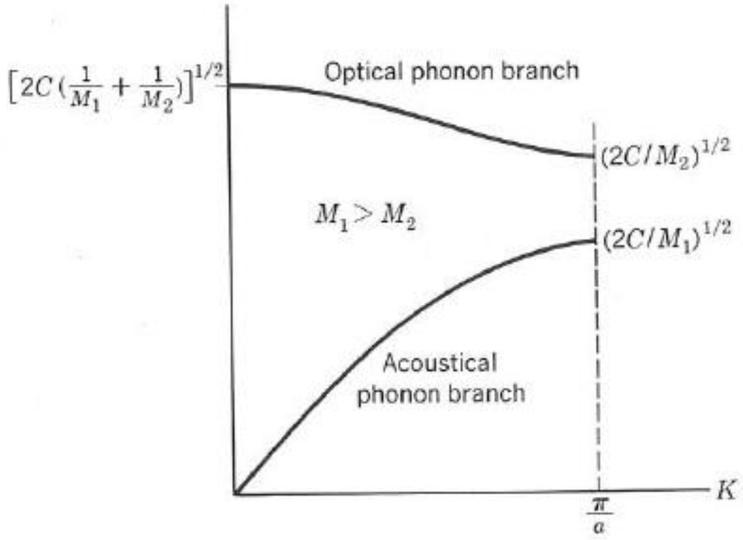


Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a.

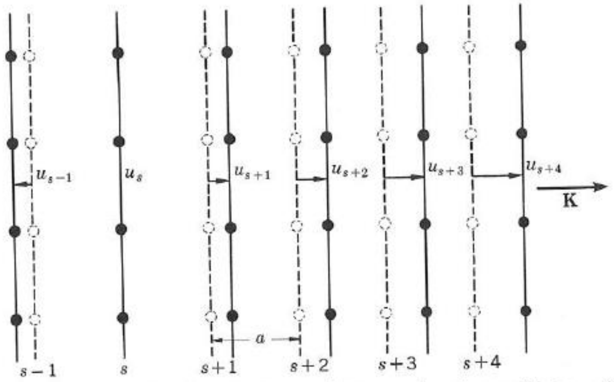


Figure 2 (Dashed lines) planes of atoms when in equilibrium. (Solid lines) planes of atoms when displaced as for a longitudinal wave. The coordinate u measures the displacement of the planes.

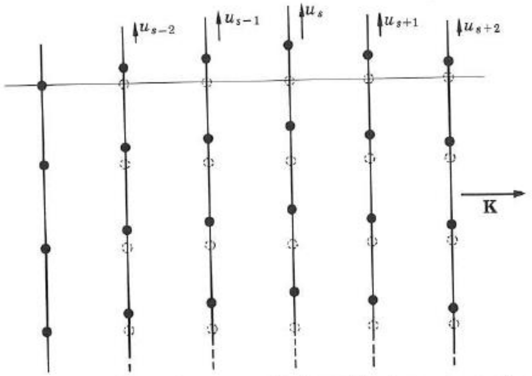


Figure 3 Planes of atoms as displaced during passage of a transverse wave.

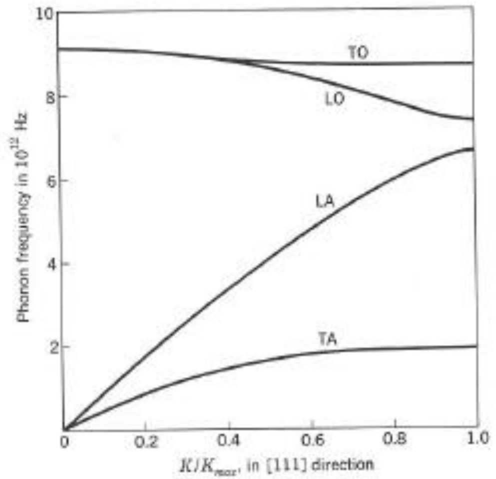


Figure 8a Phonon dispersion relations in the [111] direction in germanium at 80 K. The two TA phonon branches are horizontal at the zone boundary position, $K_{max} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The LO and TO branches coincide at $K = 0$; this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nilsson and G. Nelin, Phys. Rev. **B3**, 364 (1971).

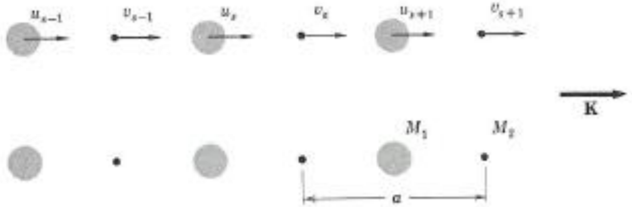


Figure 9 A diatomic crystal structure with masses M_1, M_2 connected by force constant C between adjacent planes. The displacements of atoms M_1 are denoted by $u_{s-1}, u_s, u_{s+1}, \ldots$, and of atoms M_2 by v_{s-1}, v_s, v_{s+1}. The repeat distance is a in the direction of the wavevector K. The atoms are shown in their undisplaced positions.

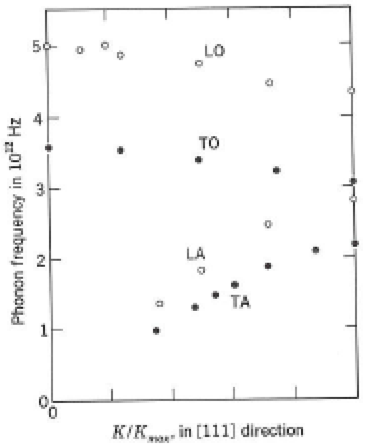


Figure 8b Dispersion curves in the [111] direction in KBr at 90 K, after A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963). The extrapolation to $K = 0$ of the TO, LO branches are called ω_T, ω_L; these are discussed in Chapter 10.

Polaritons

The coupling of the electric field E of the photon with the dielectric polarization P of the TO phonon is described by the electromagnetic wave equation:

$$\epsilon(\omega) \equiv \frac{D(\omega)}{E(\omega)} \equiv 1 + 4\pi \frac{P(\omega)}{E(\omega)}$$

(CGS) $$c^2K^2E = \omega^2(E + 4\pi P)$$

In this section we see how the coupling is responsible for the dispersion relations shown as solid curves in the figure. All of this takes place at very low values of the wavevector in comparison with a zone boundary, because at crossover $\omega(\text{photon}) = ck(\text{photon}) = \omega(\text{phonon}) \approx 10^{13}\ \text{s}^{-1}$; thus $k \approx 300\ \text{cm}^{-1}$. An early warning: Although the symbol ω_L will necessarily arise in the theory, the effects do not concern longitudinal optical phonons. Longitudinal phonons do not couple to transverse photons in the bulk of a crystal.

At low wavevectors the TO phonon frequency ω_T is independent of K. The polarization is proportional to the displacement of the positive ions relative to the negative ions, so that the equation of motion of the polarization is like that of an oscillator and may be written as, with $P = Nqu$,

$$-\omega^2P + \omega_T{}^2P = (Nq^2/M)E\ , \qquad (50)$$

where there are N ion pairs of effective charge q and reduced mass M, per unit volume. The equations (49) and (50) have a solution when

$$\begin{vmatrix} \omega^2 - c^2K^2 & 4\pi\omega^2 \\ Nq^2/M & \omega^2 - {\omega_T}^2 \end{vmatrix} = 0 \ . \tag{51}$$

This gives the polariton dispersion relation plotted in Figs. 11 and 12. At $K = 0$ there are two roots, $\omega = 0$ for the photon and

$$\omega^2 = {\omega_T}^2 + 4\pi Nq^2/M = {\omega_L}^2 \tag{52}$$

$$\epsilon(\omega) = \epsilon(\infty) + [\epsilon(0) - \epsilon(\infty)]\,\frac{{\omega_T}^2}{{\omega_T}^2 - \omega^2} = \epsilon(\infty)\left(\frac{{\omega_L}^2 - \omega^2}{{\omega_T}^2 - \omega^2}\right) \ .$$

The zero of $\epsilon(\omega)$ is at ω_L and the pole is at ω_T.

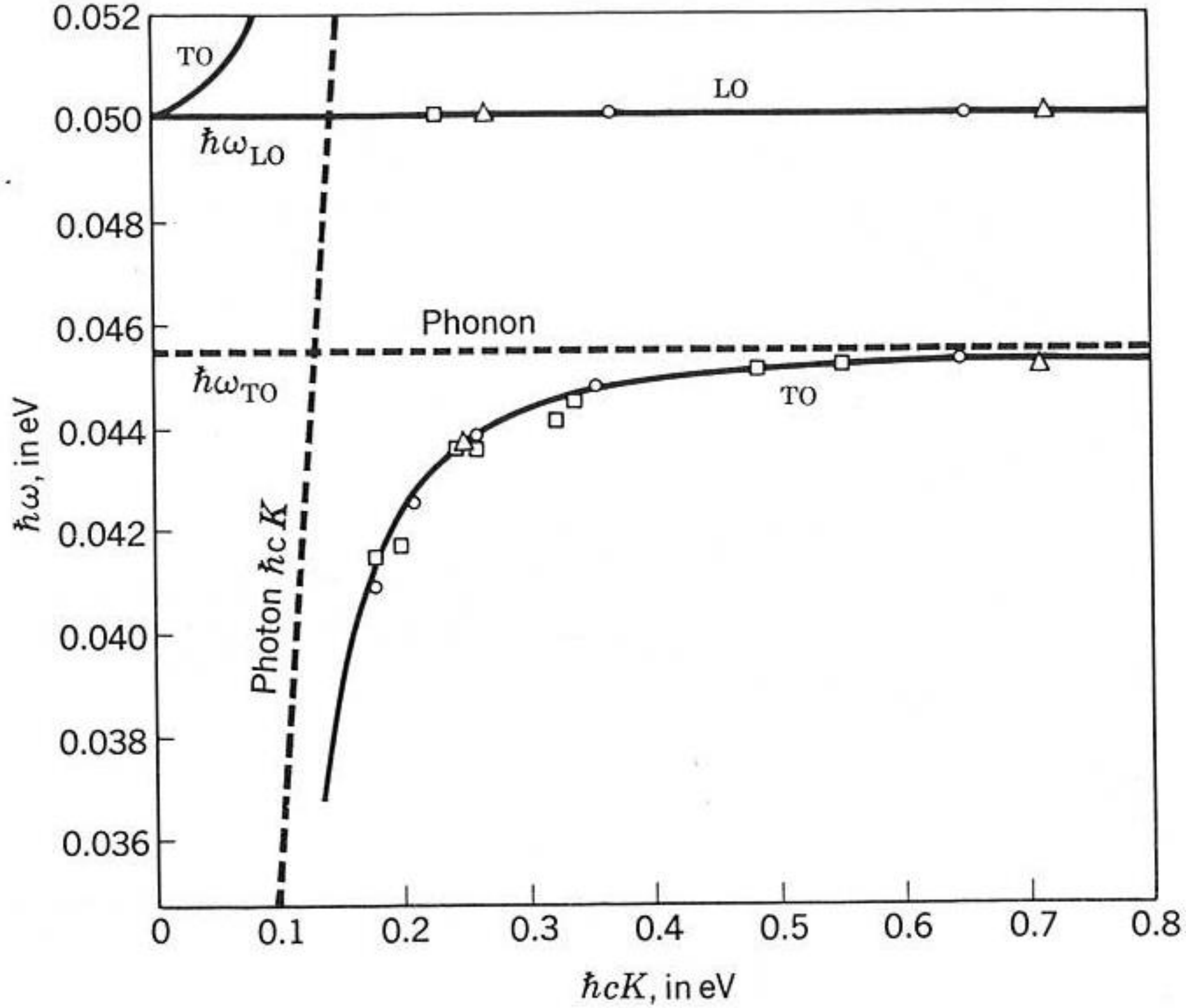
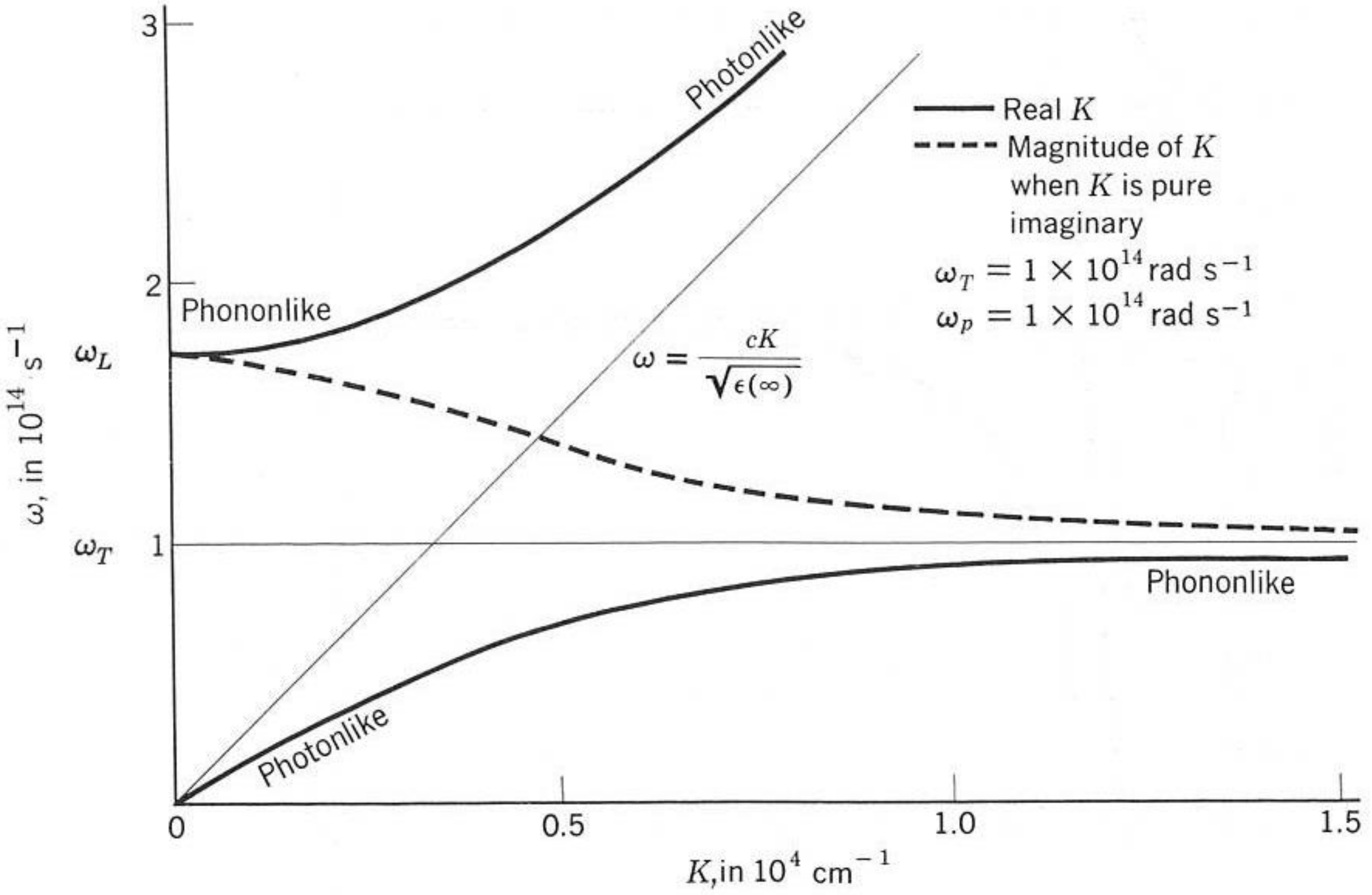
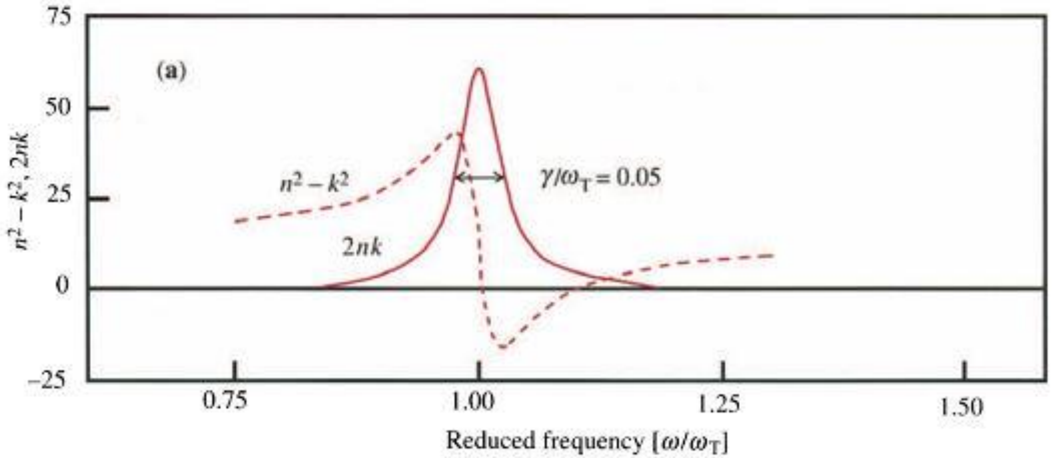
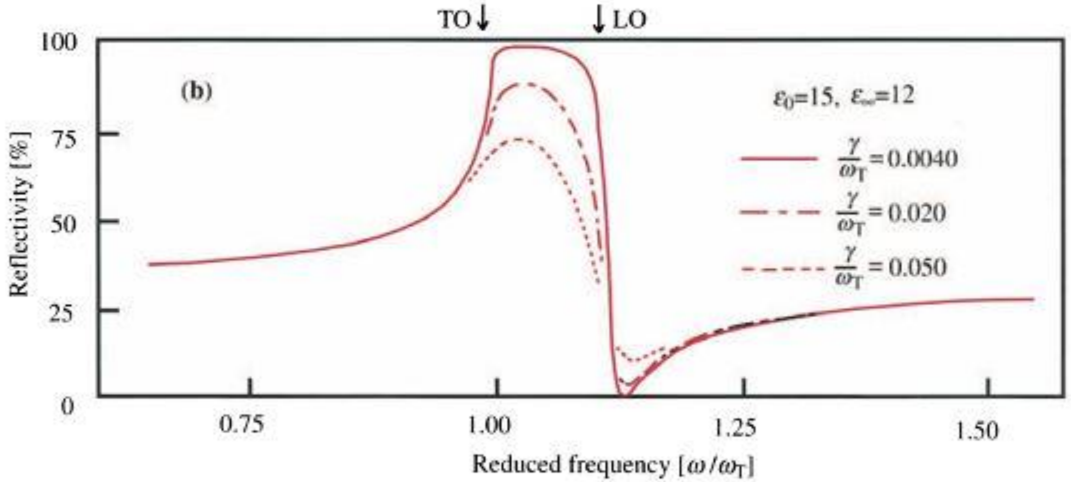


Figure 11 A plot of the observed energies and wavevectors of the polaritons and of the LO phonons in GaP. The theoretical dispersion curves are shown by the solid lines. The dispersion curves for the uncoupled phonons and photons are shown by the short, dashed lines. [After C. H. Henry and J. J. Hopfield, Phys. Rev. Letters **15,** 964 (1965).]

3
2
1
ω_L
ω_T
ω, in 10^{14} s^{-1}
0
0.5
1.0
1.5
K, in 10^4 cm^{-1}
Photonlike
Phononlike
Photonlike
Phononlike
$\omega = \frac{cK}{\sqrt{\epsilon(\infty)}}$
Real K
Magnitude of K when K is pure imaginary
$\omega_T = 1 \times 10^{14}$ rad s^{-1}
$\omega_p = 1 \times 10^{14}$ rad s^{-1}



Real and imaginary part of the complex dielectric constant calculated for a Zinc blende structure



Reflectivity coefficients calculated from different values of the damping factor γ

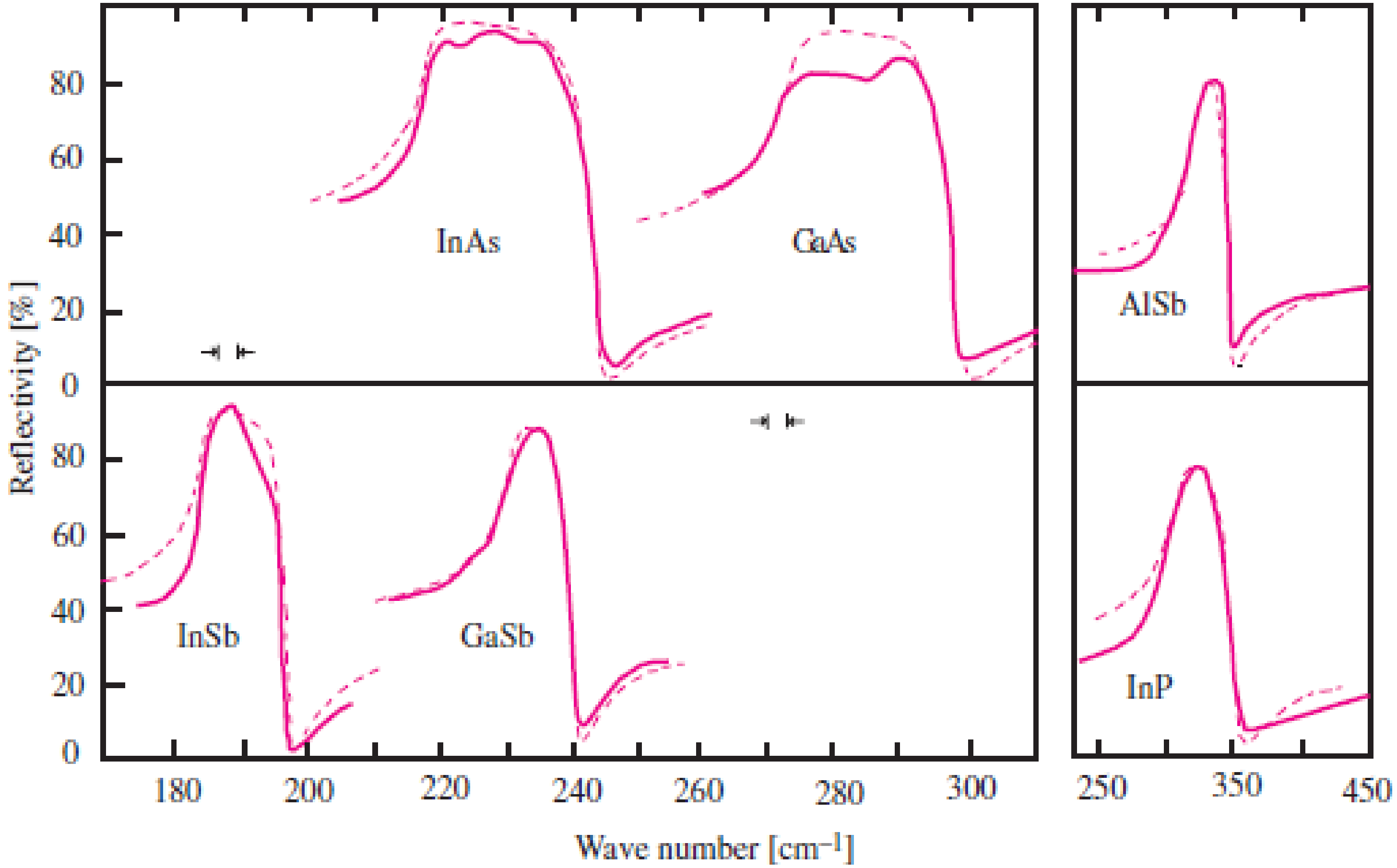


Fig. 6.32. Comparison between experimental (*solid curves*) lattice reflection spectra in several zinc-blende-type semiconductors with those calculated from (6.117b) using (6.8) (*broken curves*). The TO and LO phonon frequencies and the corresponding damping constants were adjusted to fit the experimental spectra. The spectra on the left-hand side were measured at liquid helium temperature; those on the right are room temperature spectra [6.69]

Table 6.5. The TO (ω_T) and LO phonon (ω_L) frequencies and the ratio of the damping constant (γ) to ω_T determined from lattice reflection spectra in several zinc-blende-type semiconductors [6.69] and from Raman scattering [6.72]

Semiconductor	Temperature [K]	ω_T [cm^{-1}]	ω_L [cm^{-1}]	γ/ω_T
InSb	4.2	184.7	197.2	<0.01
	300	179.1	190.4	0.016
InAs	4.2	218.9	243.3	<0.01
InP	300	307.2	347.5	0.01
GaSb	4.2	230.5	240.3	<0.01
GaAs	4.2	273.3	297.3	<0.01
	296	268.2	291.5	0.007
GaP	300	366.3	401.9	0.003
GaN	300	555	740	–
AlSb	300	318.8	339.6	0.0059
CdTe	1.2	145	170	–
ZnSe	80	211	257	0.01

Hagen–Rubens Relation

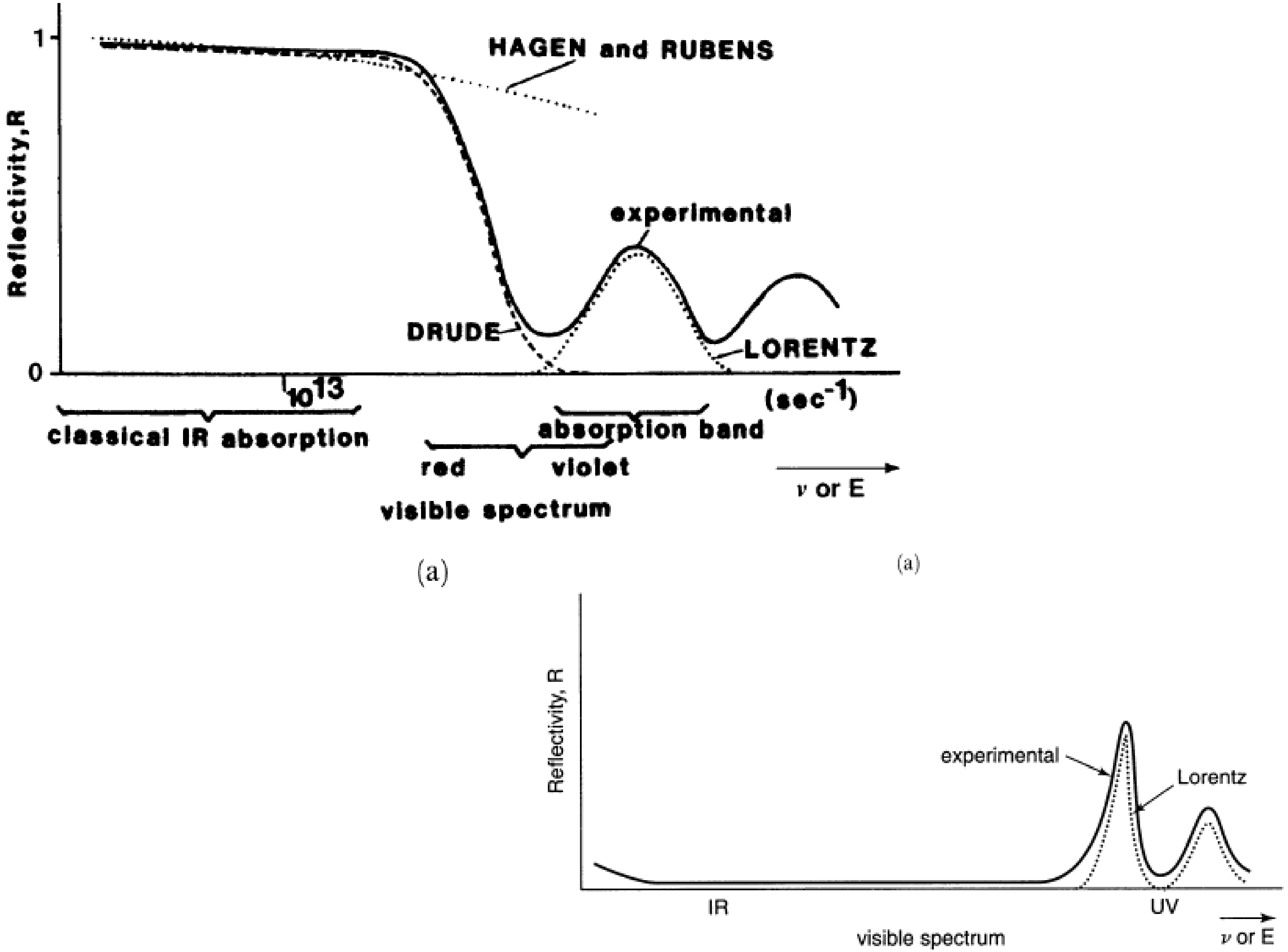
Our next task is to find a relationship between reflectivity and conductivity. For small frequencies (i.e., $\nu < 10^{13}\ \mathrm{s}^{-1}$) the ratio $\sigma/2\pi\varepsilon_0\nu$ for metals is very large, that is, $\sigma/2\pi\varepsilon_0 \approx 10^{17}\ \mathrm{s}^{-1}$. With $\varepsilon \approx 10$ we obtain

$$\frac{\sigma}{2\pi\varepsilon_0\nu} \approx \frac{10^{17}}{10^{13}} \gg \varepsilon.$$

$$\boxed{R = 1 - 4\sqrt{\frac{\nu}{\sigma_0}\pi\varepsilon_0},}$$

which states that in the infrared (IR) region metals with large electrical conductivity are good reflectors. This equation was found empirically by Hagen and Rubens from reflectivity measurements in the IR and was derived theoretically by Drude. As stated above, the Hagen–Rubens relation is only valid at frequencies below $10^{13}\ \mathrm{s}^{-1}$ or, equivalently, at wavelengths larger than about 30 μm.

REAL MATERIALS



(a)

(a)

(b)

Figure 11.1. Schematic frequency dependence of the reflectivity of (a) metals, (b) dielectrics, experimentally (solid line) and according to three models.

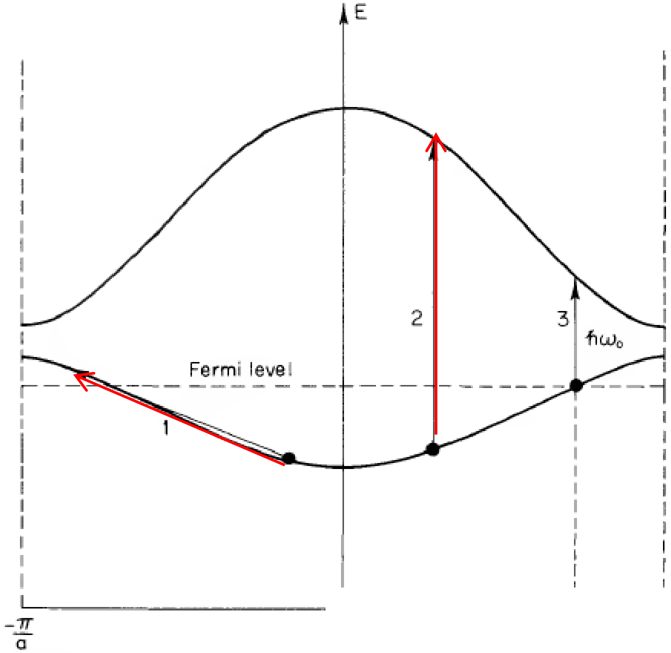
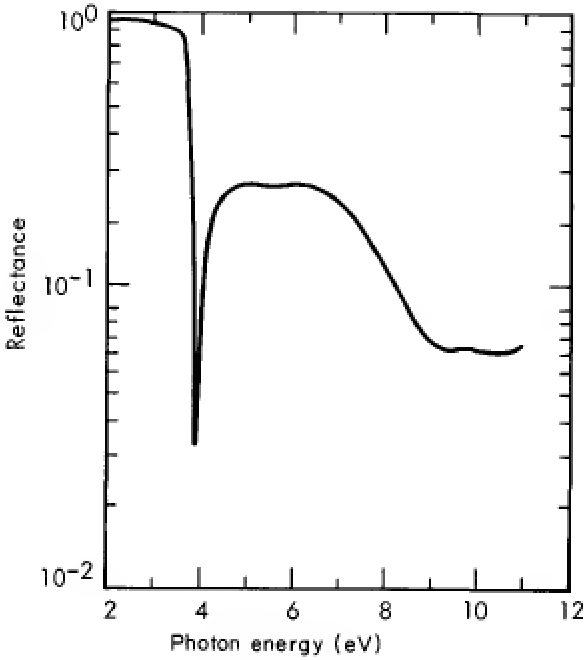


Fig. 3.14 A schematic band diagram fo
from the Fermi energy at $\mathbf{k}_0$ to the same st

1 Intraband transition
2 Direct interband transition

Fig. 3.15 Reflectance of Ag. [From G. B. Irani, T. Huen, and F. Wooten, *Phys. Rev.* **3B**, 2385 (1971).]



The sharp decrease in reflectance at ~ 3.9 eV is
Interpreted as an identification of the plasma frequency

Kramers-Kronig relations associate real and imaginary refraction indexes of a material. These are called optical constant, even if they strongly depend upon the wavelength an daccording to the characteristics of the medium.

The real part of the index (generally called index of refraction) ids what we find in the Snell-Descartes laws, the imaginary part (absorption coefficient) describing the absorption during the propagation in the medium. The simultaneous measurements of both quantities is a difficult task, the Kramers-Kronig relations allow to calculate one by knowing the other, therefore being of primary importance in spectroscopy.

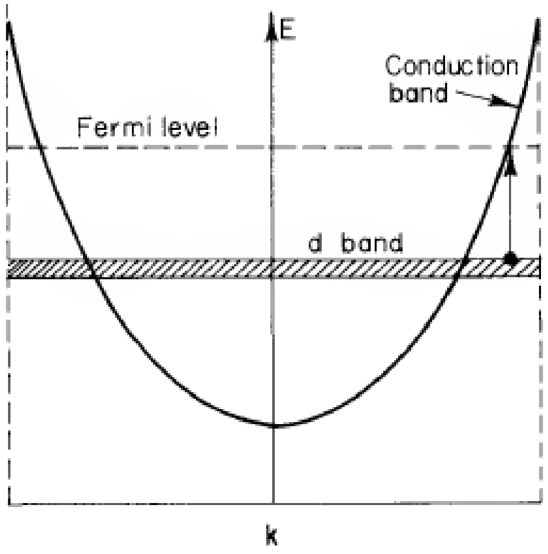
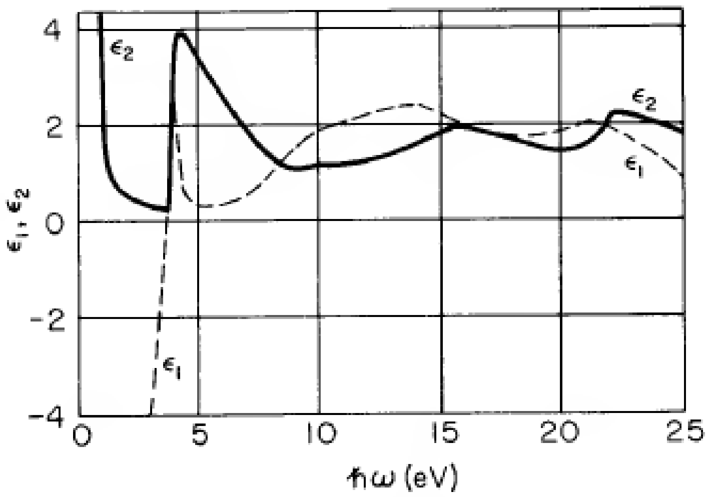


Fig. 3.16 Schematic band diagram for the noble metals.

Fig. 3.17 Spectral dependence of the real and imaginary dielectric functions for Ag. [From H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).]



The e
contribution to $\varepsilon_1$and also a rise to ε_2.

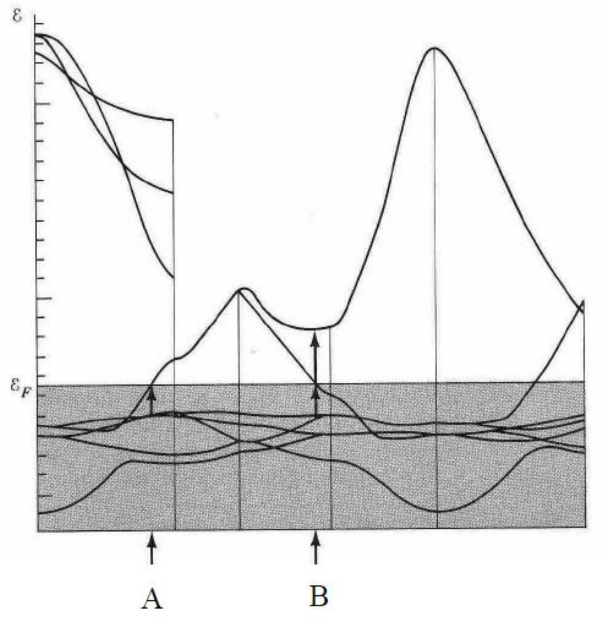
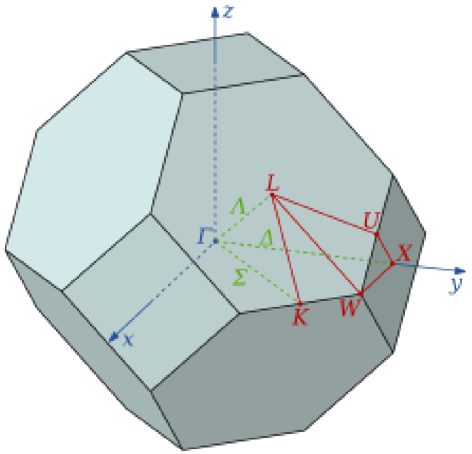


Fig.5 Calculated bands for copper, illustrating that the absorption threshold for transitions up from the conduction band is about 4 eV, while the threshold for transitions from the d-band to the conduction band is only about 2 eV. The energy scale is in tenths of a rydberg (0.1 Ry = 1.36 eV).



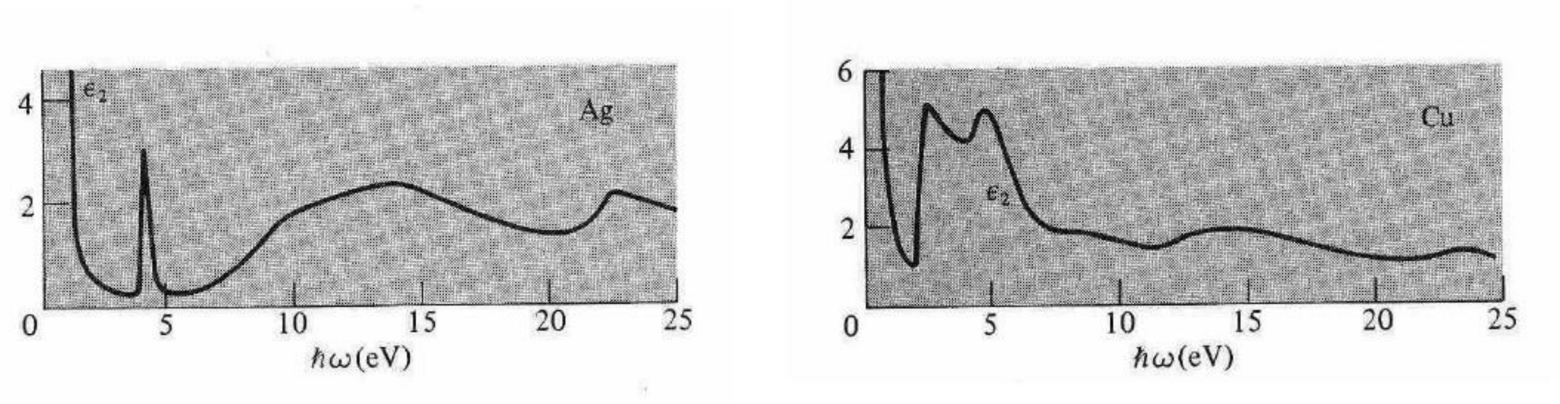


Fig.6 The imaginary part of the dielectric constants deduced from reflectivity measurements. (H. Ehrenreich and H. R. Phillip, *Phys. Rev.* 128, 1622 (1962).) Note the characteristic free electron behavior ($1/\omega^3$) below about 2 eV in copper and below about 4 eV in silver. The onset of interband absorption is quite apparent.

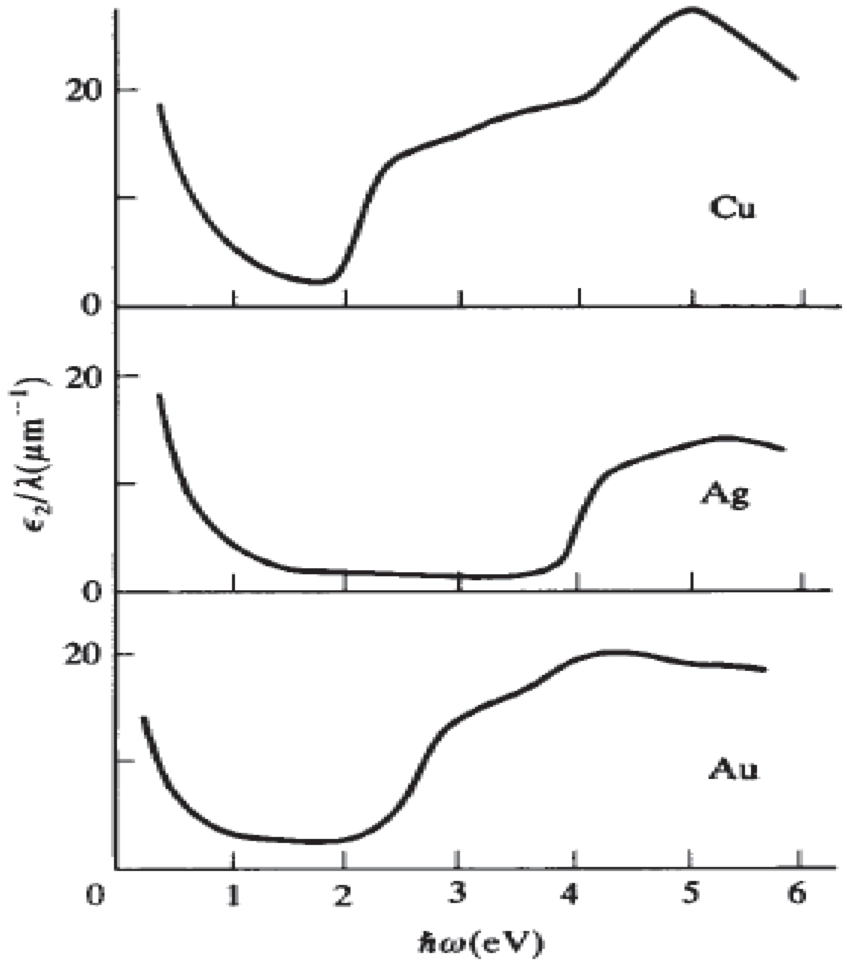


Figure 9.17 In the coinage metals the d band is filled and therefore lies below the Fermi level. The optical spectra are dominated by the Drude absorption at low energies. The interband absorption begins abruptly at 'edges' that arise primarily in transitions from the flat top of the filled d band to the empty states just above the Fermi energy. At still higher photon energies, spectral structure develops on account of several vertical transitions between filled and empty states; see Fig. 9.18 for more detail.

Cu [Ar] $3d^{10}4s^1$

Ag [Kr] $4d^{10}5s^1$

Au [Xe] $4f^{14}5d^{10}6s^1$

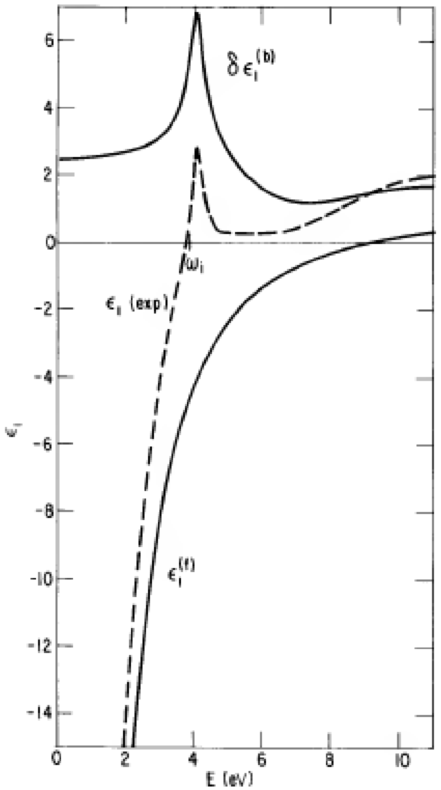


Fig. 3.18 Decomposition of the experimental values of $\varepsilon_1(\omega)$ for Ag into free and bound contributions $\varepsilon_1^{(f)}$ and $\delta\varepsilon_1^{(b)}$. The threshold energy for interband transitions is indicated by ω_i. [From H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).]

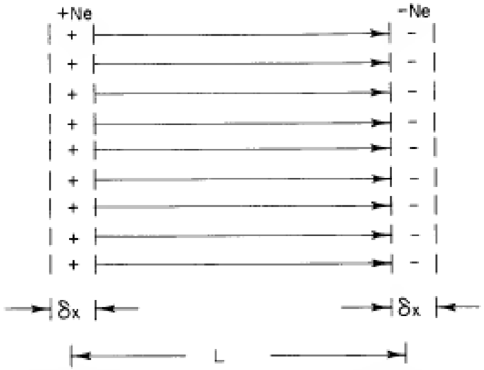


Fig. 3.19 Schematic diagram of the origin of plasma oscillations in one dimension. The equilibrium concentration of electrons is N. The net charge is zero because of a uniform background density of positive ions. Now, imagine that a region of electron charge has been uniformly translated a distance δx without disturbing the rest of the system. This leaves a region of thickness δx having a net positive charge density and creates another region of net negative charge density as illustrated in the figure. Because of the force between the two regions of unbalanced charge, they will be attracted toward each other. In the absence of a damping mechanism, there will be an overshoot, leading to the situation depicted in the figure, but with the charges reversed. The system will continue to oscillate in this manner at a characteristic frequency known as the plasma frequency. The oscillations are called plasma oscillations. The plasma frequency can be easily derived for this simple case. Recognizing that the polarization is the dipole moment per unit volume, we have

$$\mathbf{P} = -(NeA\,\delta x)L/AL = -Ne\,\delta x$$

In the absence of an external field, this gives rise to the total electric field

$$\mathbf{E} = -4\pi\mathbf{P} = 4\pi Ne\,\delta x$$

The force on an electron in the polarized region is thus

$$m\ddot{x} = -e\mathbf{E} = -4\pi Ne^2\,\delta x$$

This is just the equation for a simple harmonic oscillator with characteristic frequency

$$\omega_p^2 = 4\pi Ne^2/m$$

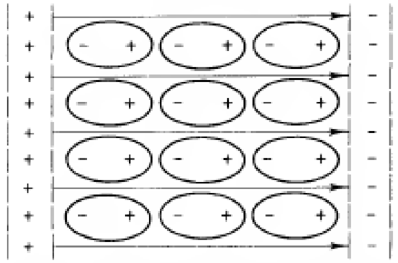


Fig. 3.20 Screening of plasma oscillations by polarization of localized electrons. Compare with Fig. 3.19. The d electrons are highly localized on atomic sites. However, their polarizability may be high enough to cause appreciable screening of the forces between fluctuations in the charge densities of conduction electrons. The result can be a significant shift in the plasma frequency.

$$I_0 = I_T + I_A + I_R \tag{21.4}$$

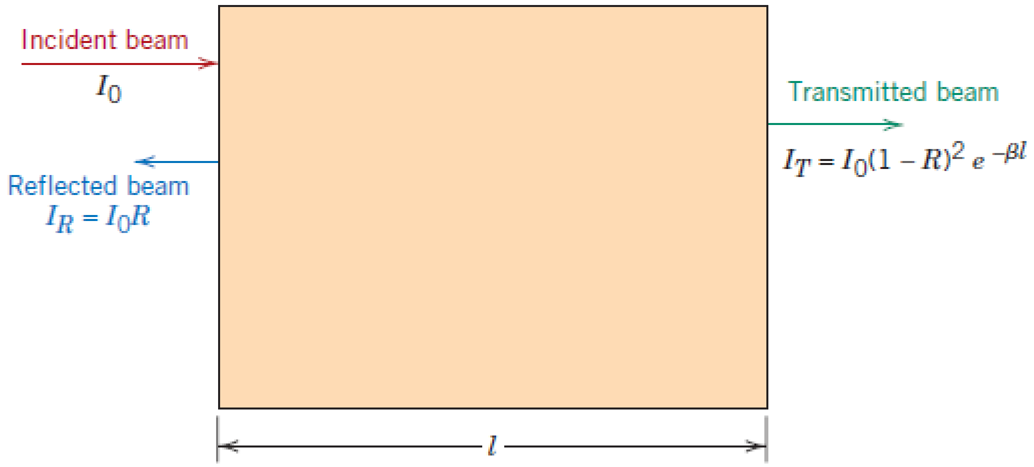
Radiation intensity, expressed in watts per square meter, corresponds to the energy being transmitted per unit of time across a unit area that is perpendicular to the direction of propagation.

An alternate form of Equation 21.4 is

$$T + A + R = 1 \tag{21.5}$$

where T, A, and R represent, respectively, the transmissivity (I_T/I_0), absorptivity (I_A/I_0), and reflectivity (I_R/I_0), or the fractions of incident light that are transmitted, absorbed, and reflected by a material; their sum must equal unity, since all the incident light is either transmitted, absorbed, or reflected.

Figure 21.7 The transmission of light through a transparent medium for which there is reflection at front and back faces, as well as absorption within the medium. (Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, *The Structure and Properties of Materials*, Vol. 4, *Electronic Properties.* Copyright © 1966 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



$$I_T = I_0(1 - R)^2 e^{-\beta l}$$

$$R + T + A = 1$$

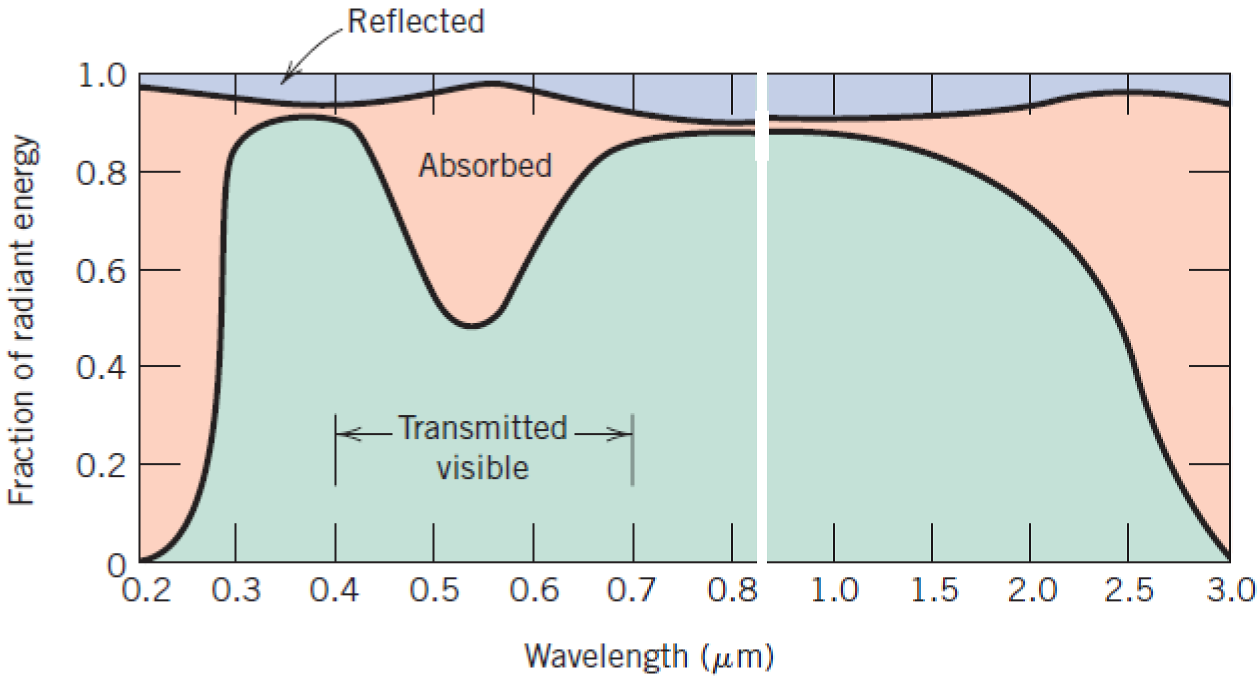


Figure 21.8 The variation with wavelength of the fractions of incident light transmitted, absorbed, and reflected through a green glass. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

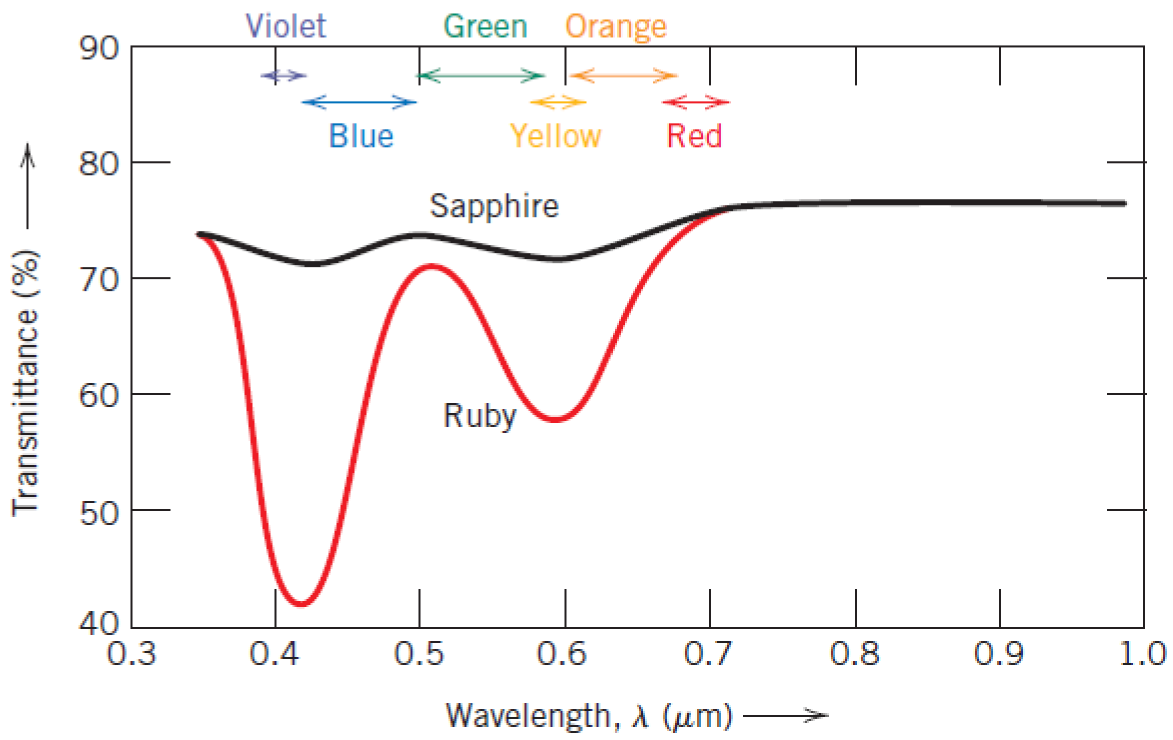


Figure 21.9 Transmission of light radiation as a function of wavelength for sapphire (single-crystal aluminum oxide) and ruby (aluminum oxide containing some chromium oxide). The sapphire appears colorless, while the ruby has a red tint due to selective absorption over specific wavelength ranges. (Adapted from "The Optical Properties of Materials," by A. Javan. Copyright © 1967 by Scientific American, Inc. All rights reserved.)

DIELECTRIC MATERIALS

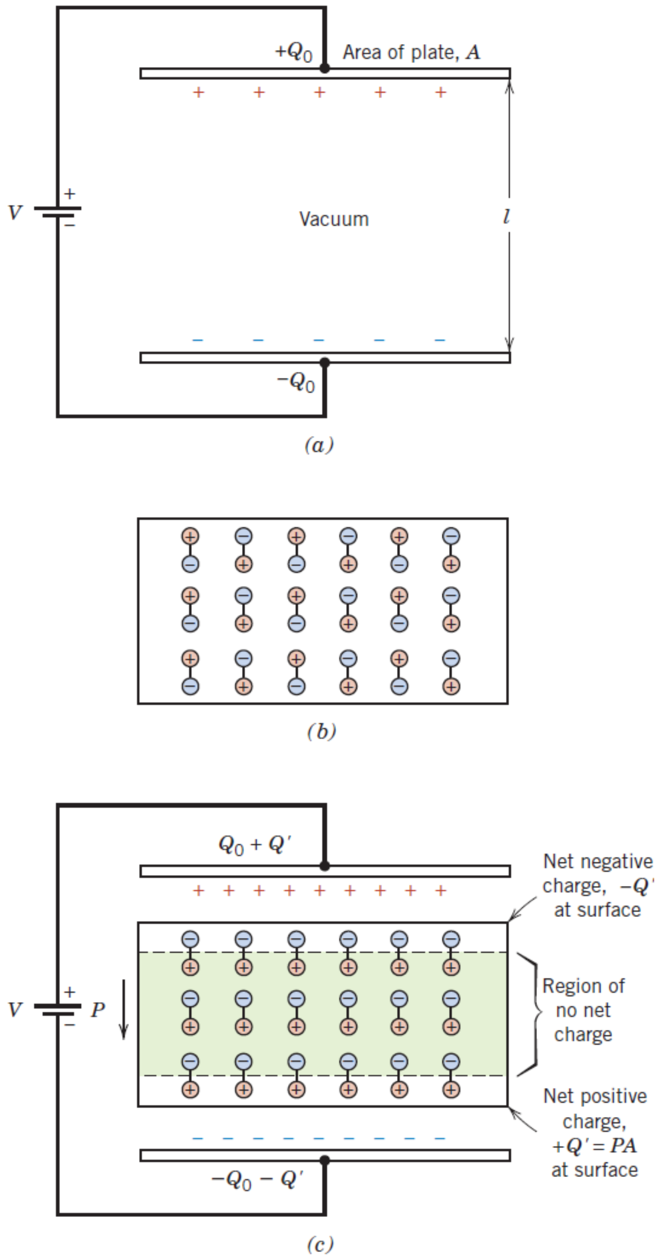


Figure 18.31 Schematic representations of (*a*) the charge stored on capacitor plates for a vacuum, (*b*) the dipole arrangement in an unpolarized dielectric, and (*c*) the increased charge storing capacity resulting from the polarization of a dielectric material. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976.)

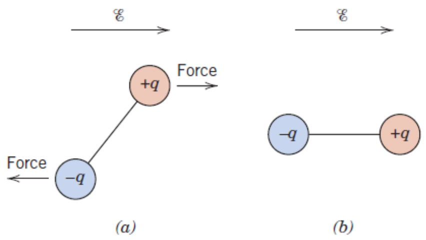


Figure 18.30 (*a*) Imposed forces (and torque) acting on a dipole by an electric field. (*b*) Final dipole alignment with the field.

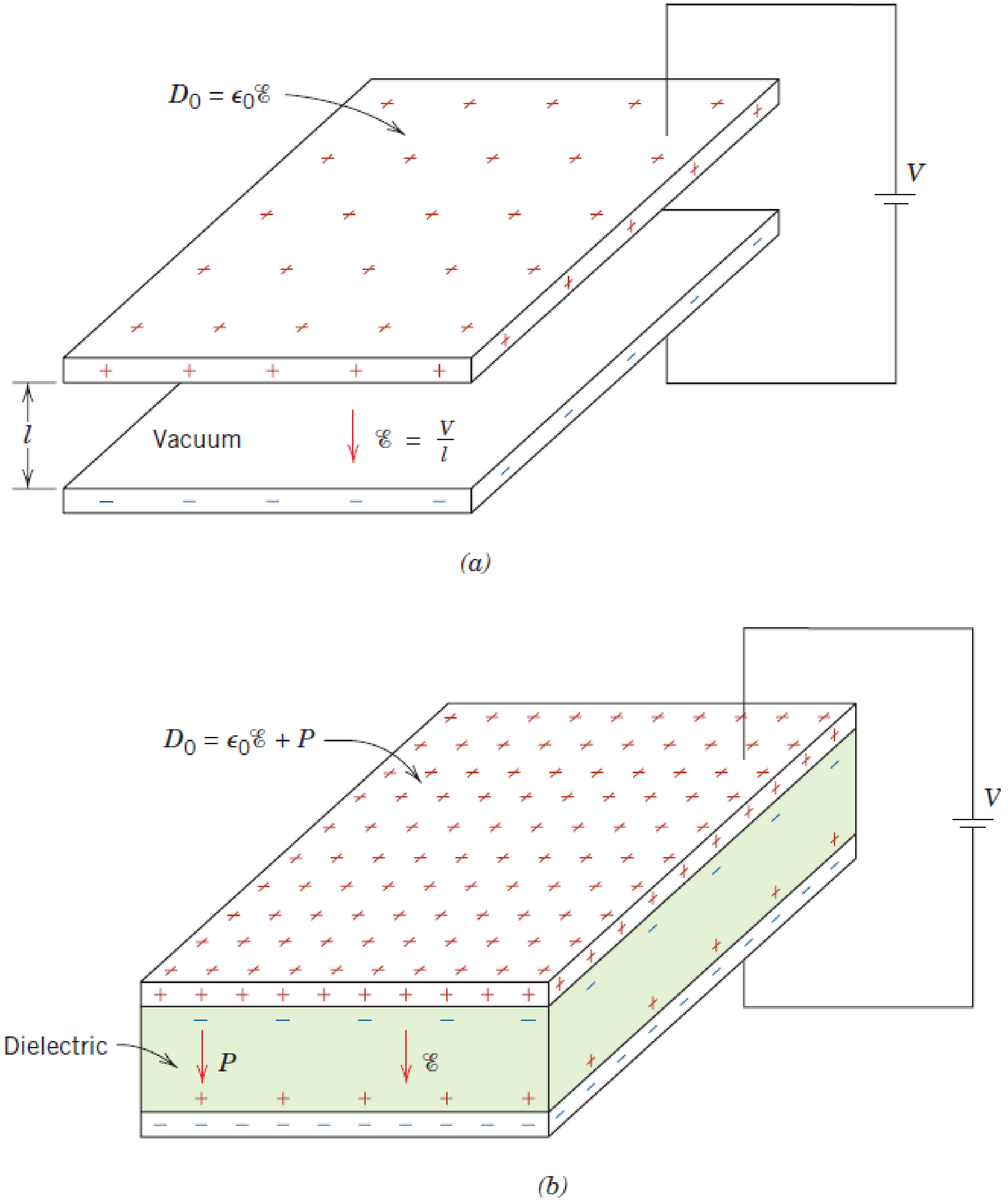


Figure 18.28 A parallel-plate capacitor (*a*) when a vacuum is present and (*b*) when a dielectric material is present. (From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

Table 18.5 **Dielectric Constants and Strengths for Some Dielectric Materials**

Material	*Dielectric Constant*		*Dielectric Strength (V/mil)*[a]
	60 Hz	*1 MHz*	
	Ceramics		
Titanate ceramics	—	15–10,000	50–300
Mica	—	5.4–8.7	1000–2000
Steatite ($MgO–SiO_2$)	—	5.5–7.5	200–350
Soda–lime glass	6.9	6.9	250
Porcelain	6.0	6.0	40–400
Fused silica	4.0	3.8	250
	Polymers		
Phenol-formaldehyde	5.3	4.8	300–400
Nylon 6,6	4.0	3.6	400
Polystyrene	2.6	2.6	500–700
Polyethylene	2.3	2.3	450–500
Polytetrafluoroethylene	2.1	2.1	400–500

[a] One mil = 0.001 in. These values of dielectric strength are average ones, the magnitude being dependent on specimen thickness and geometry, as well as the rate of application and duration of the applied electric field.

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

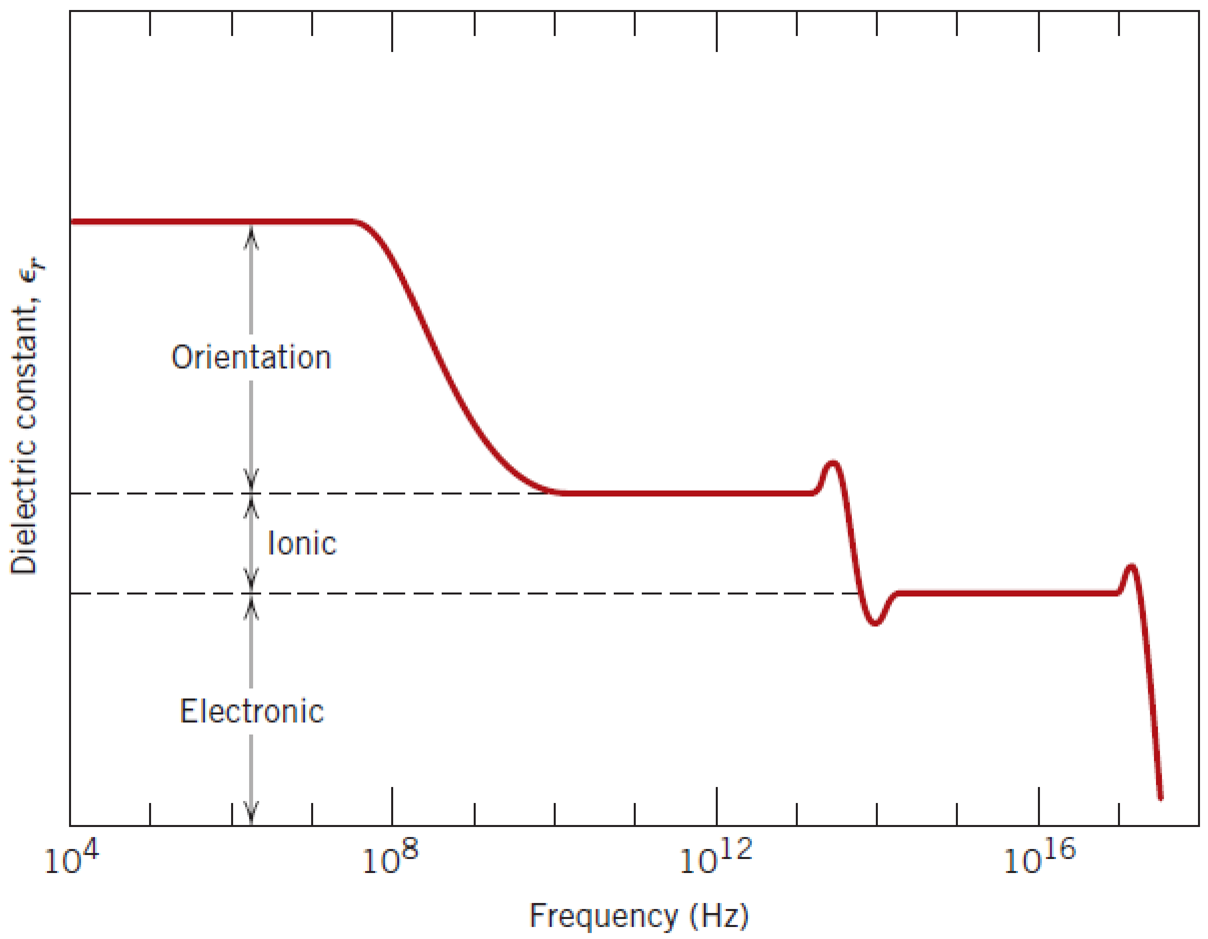


Figure 18.34 Variation of dielectric constant with frequency of an alternating electric field. Electronic, ionic, and orientation polarization contributions to the dielectric constant are indicated.

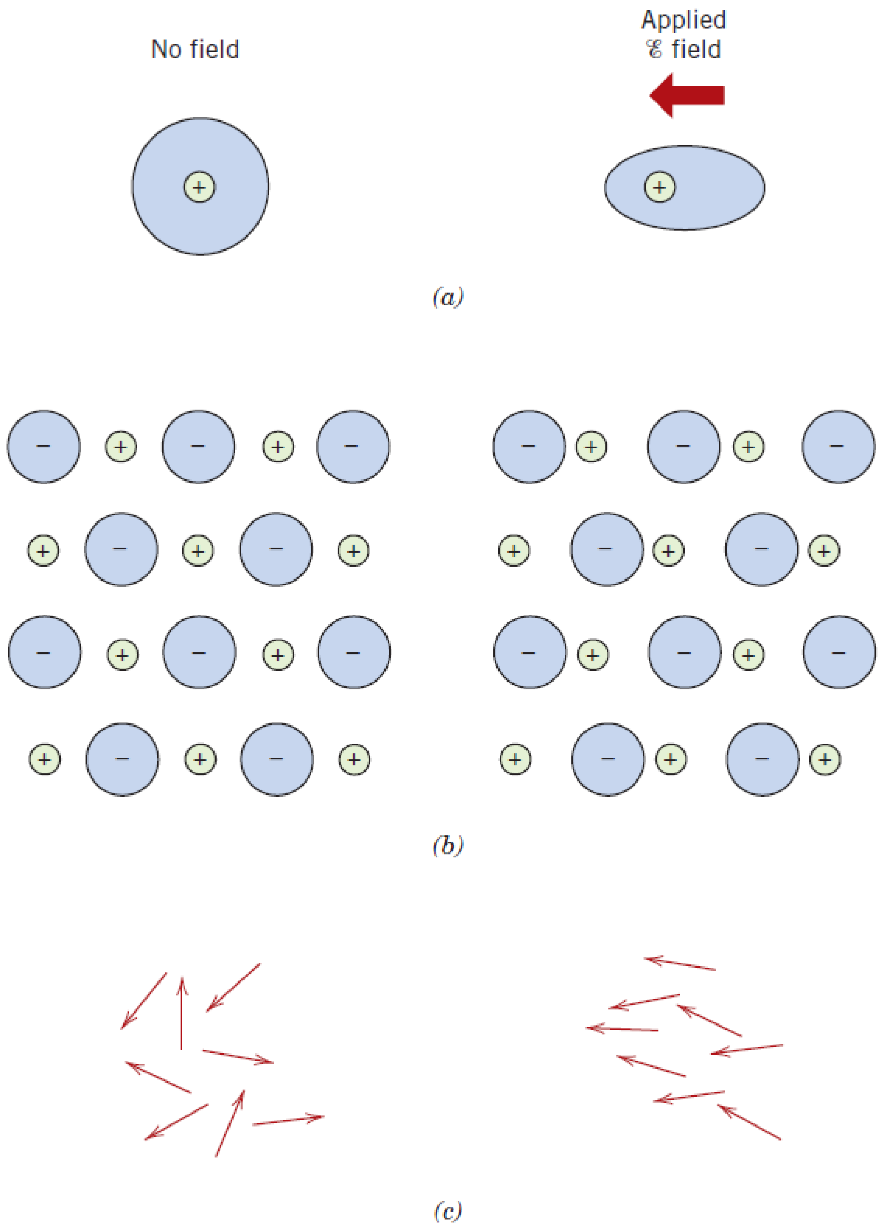
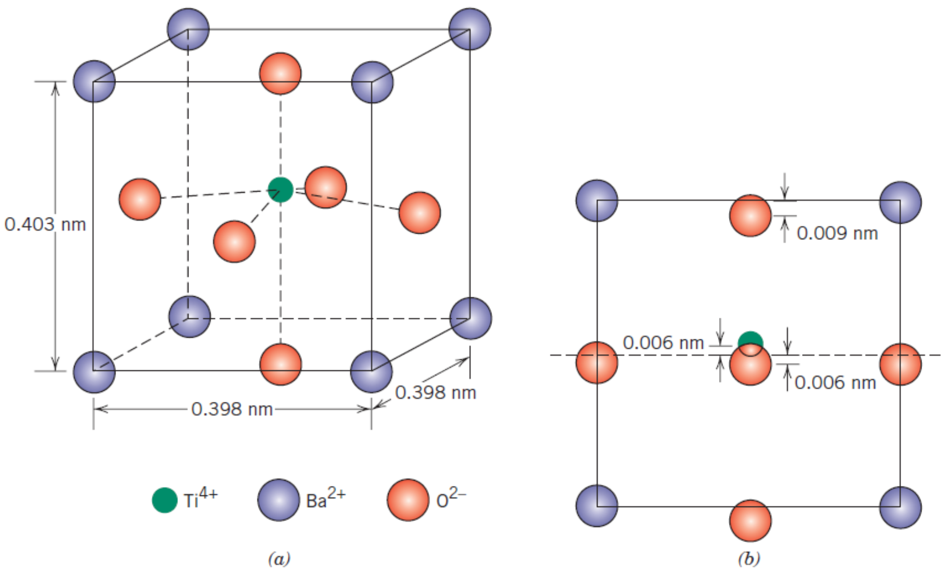


Figure 18.32 (*a*) Electronic polarization that results from the distortion of an atomic electron cloud by an electric field. (*b*) Ionic polarization that results from the relative displacements of electrically charged ions in response to an electric field. (*c*) Response of permanent electric dipoles (arrows) to an applied electric field, producing orientation polarization. (From O. H. Wyatt and D. Dew-Hughes, *Metals, Ceramics and Polymers,* Cambridge University Press, 1974.)

FERROECTRIC MATERIALS

Figure 18.35 A barium titanate ($BaTiO_3$) unit cell (*a*) in an isometric projection, and (*b*) looking at one face, which shows the displacements of Ti^{4+} and O^{2-} ions from the center of the face.



Spontaneous polarization of this group of materials results as a consequence of interactions between adjacent permanent dipoles wherein they mutually align, all in the same direction. For example, with barium titanate, the relative displacements of O^{2-} and Ti^{4+} ions are in the same direction for all the unit cells within some volume region of the specimen. Other materials display ferroelectricity; these include Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$), potassium dihydrogen phosphate (KH_2PO_4), potassium niobate ($KNbO_3$), and lead zirconate–titanate ($Pb[ZrO_3, TiO_3]$). Ferroelectrics have extremely high dielectric constants at relatively low applied field frequencies; for example, at room temperature, ϵ_r for barium titanate may be as high as 5000. Consequently, capacitors made from these materials can be significantly smaller than capacitors made from other dielectric materials.

An unusual property exhibited by a few ceramic materials is piezoelectricity, or, literally, pressure electricity: polarization is induced and an electric field is established across a specimen by the application of external forces. Reversing the sign of an external force (i.e., from tension to compression) reverses the direction of the field. The piezoelectric effect is demonstrated in Figure 18.36. This phenomenon and examples of its application were discussed in the Materials of Importance piece that follows Section 13.8.

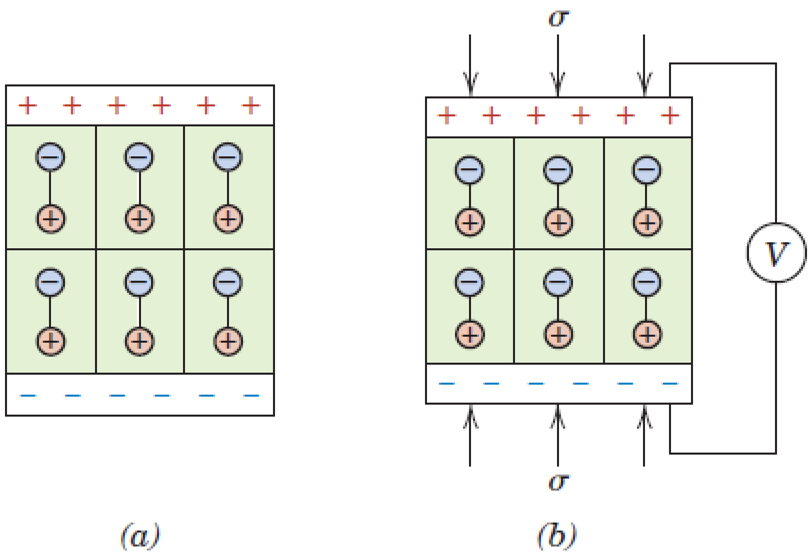


Figure 18.36 (*a*) Dipoles within a piezoelectric material. (*b*) A voltage is generated when the material is subjected to a compressive stress. (From Van Vlack, Lawrence H., *Elements of Materials Science and Engineering*, © 1989, p. 482. Adapted by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.)

Piezoelectric materials are utilized in transducers, which are devices that convert electrical energy into mechanical strains, or vice versa. Some other familiar applications that employ piezoelectrics include phonograph cartridges, microphones, speakers, audible alarms, and ultrasonic imaging. In a phonograph cartridge, as the stylus traverses the grooves on a record, a pressure variation is imposed on a piezoelectric material located in the cartridge, which is then transformed into an electric signal and is amplified before going to the speaker.

Piezoelectric materials include titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and quartz. This property is characteristic of materials having complicated crystal structures with a low degree of symmetry. The piezoelectric behavior of a polycrystalline specimen may be improved by heating above its Curie temperature and then cooling to room temperature in a strong electric field.

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