Aalto University
School of Science

PHYS-E0421 Solid State Physics
Period V, spring 2019

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Dielectric Properties of Solids
Magnetism
(Superconductivity)

Lecture 11, Monday 29.4.2019

Dielectric properties of solids

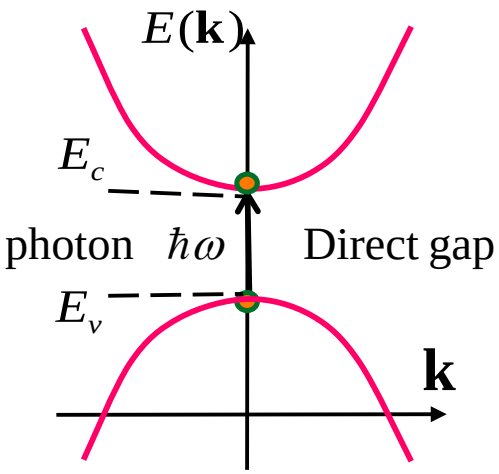
- Response of materials to an external electric field
- Optical properties of ionic solids: Light – optical phonon interactions
- Measuring light – phonon interaction
- Optical properties of electrons in solids
  - Interband transitions, excitons

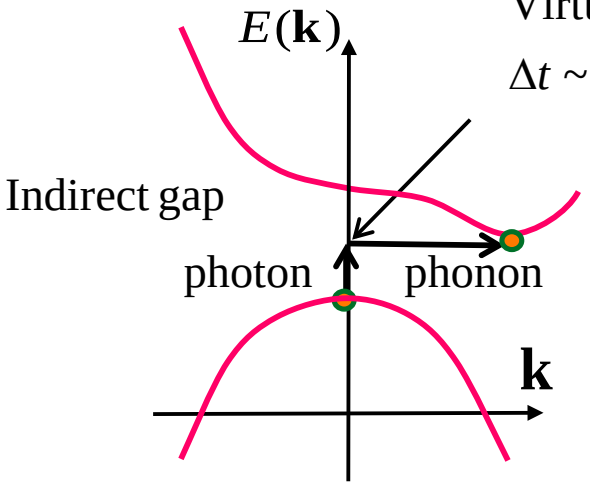
TODAY

- Response of materials to an external electric field, Summary
- Spontaneous polarization
  - Polarization is ill-defined
  - Piezoelectric, pyroelectric, ferroelectric materials → nanoelectronics

Optical Properties of Solids,
Electron Contribution to $\varepsilon(\omega)$ Interband Transitions (5.8.2)

E.g. electron - hole excitations in semiconductors





Virtual excited state

$\Delta t \sim h / \Delta E > 0$ (Heisenberg principle)

~Spherical symmetry for states around nuclei ➔ s-, p-, d- … like bands

Selection rules

$\Delta l = \pm 1$ for electric - dipole - allowed transitions

$E_f = E_i + \hbar\omega_{photon} \pm \hbar\omega_{phonon}$

$\mathbf{k}_f = \mathbf{k}_i + (\mathbf{k}_{photon}) \pm \mathbf{k}_{phonon}$

~0

Often E_v consists of s - like states

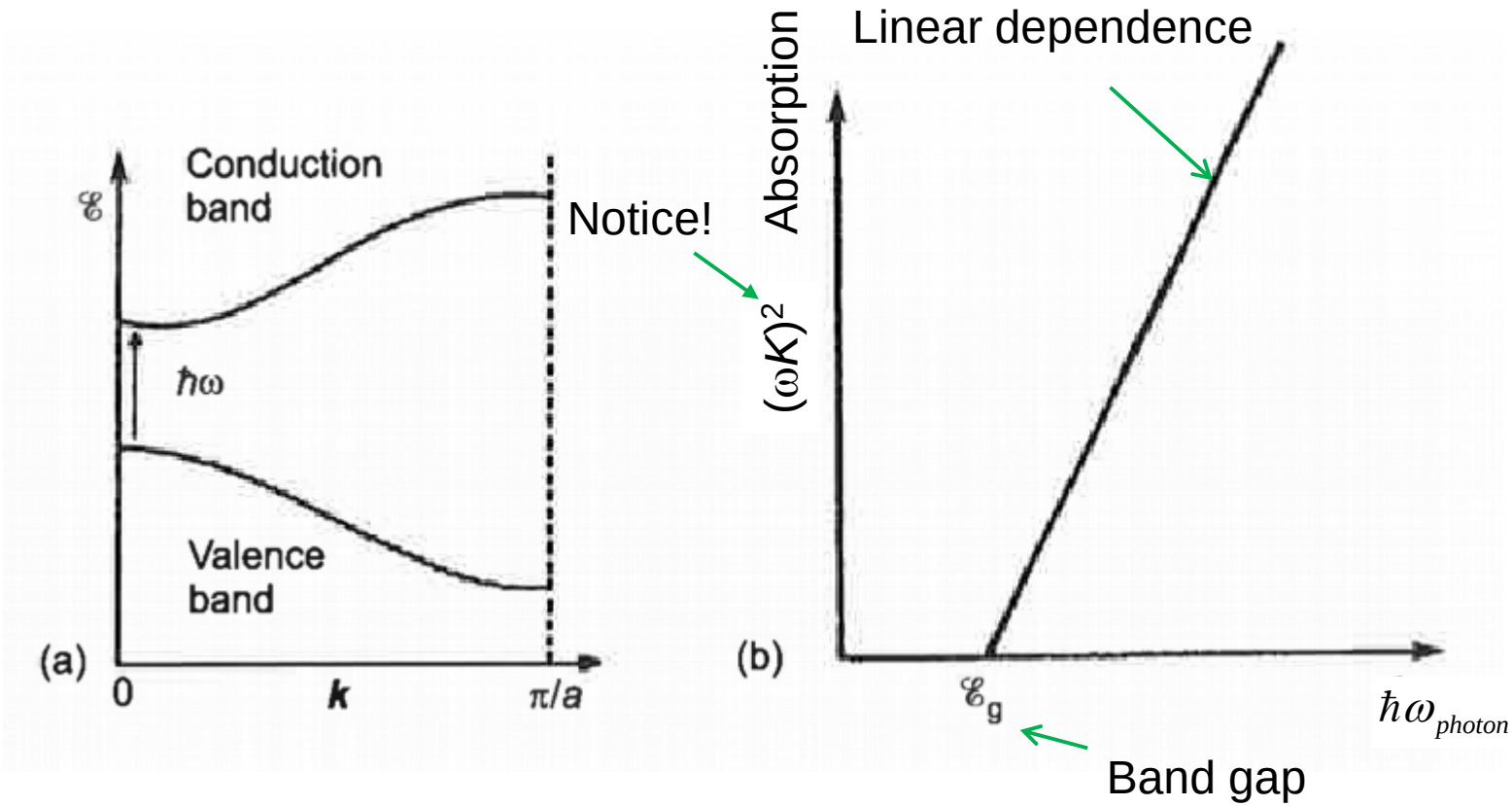
$\Rightarrow$ excitations are to p - like states at E_c

Interband Transitions

Vertical transitions

$$E_f = E_i + \hbar\omega_{photon}$$
$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{k}_{photon}$$

Direct-band-gap material



Interband Transitions

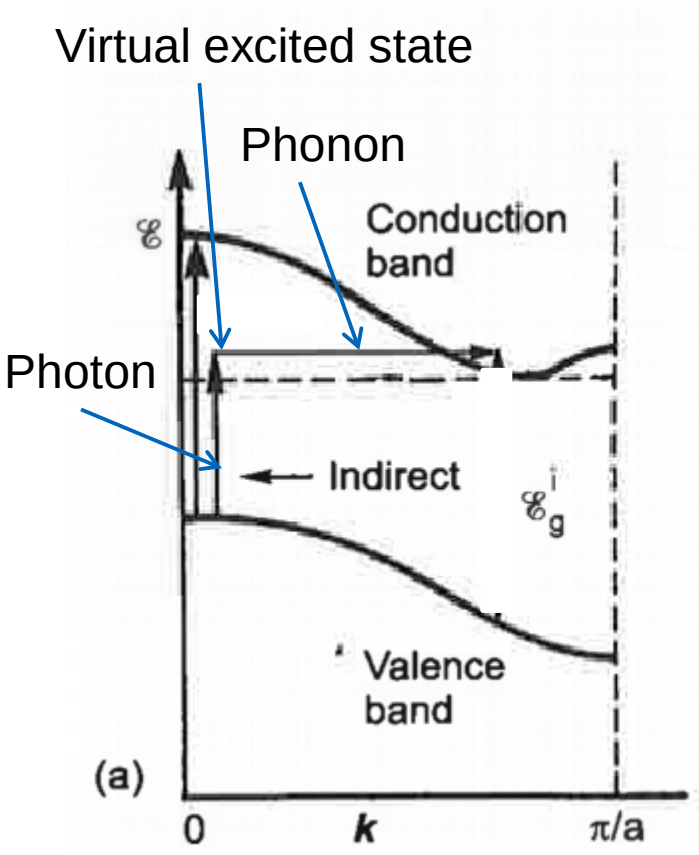
Indirect-band-gap material

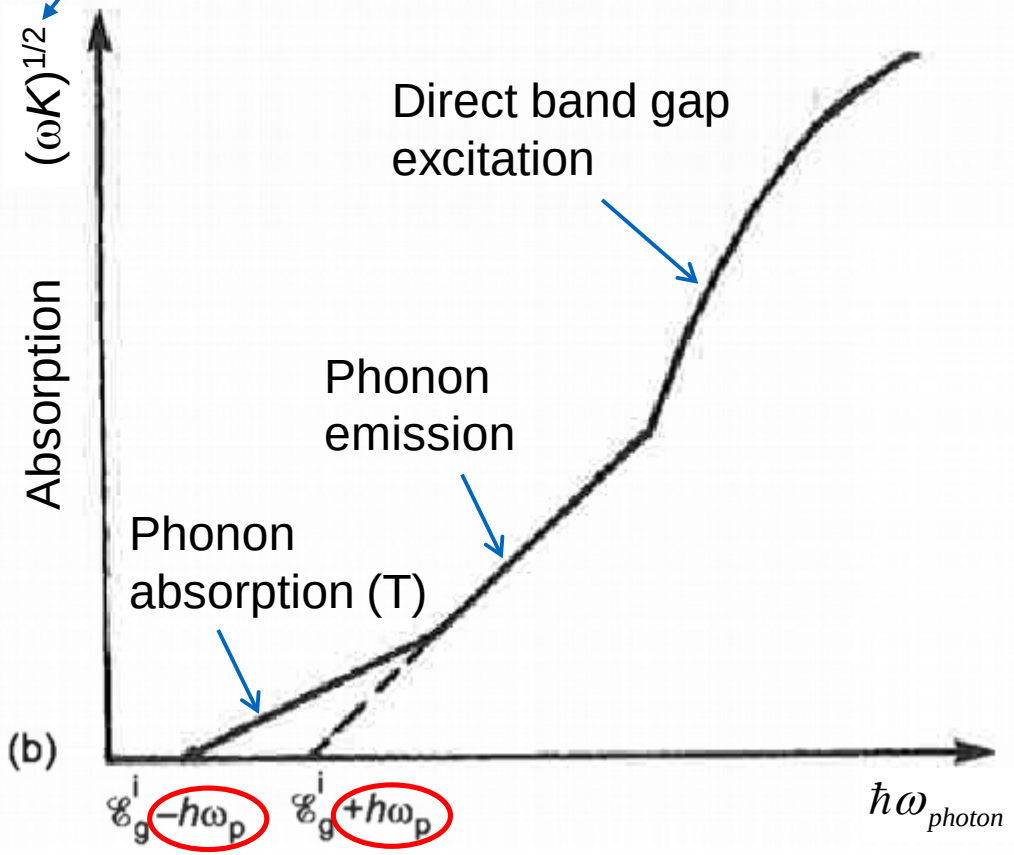
Transitions

$$E_f = E_i + \hbar\omega_{photon} \pm \hbar\omega_{phonon}$$

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{k}_{photon} \pm \mathbf{k}_{phonon}$$

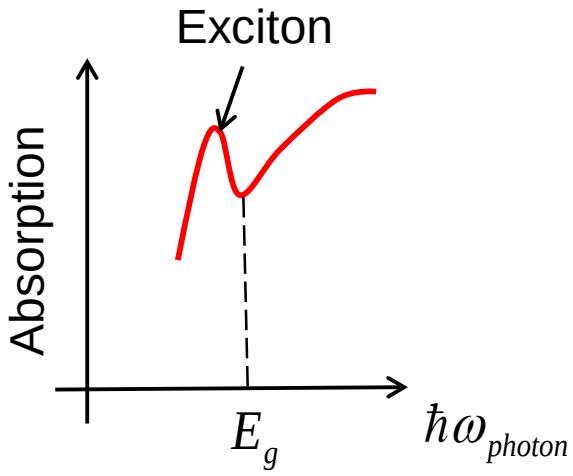
Notice!



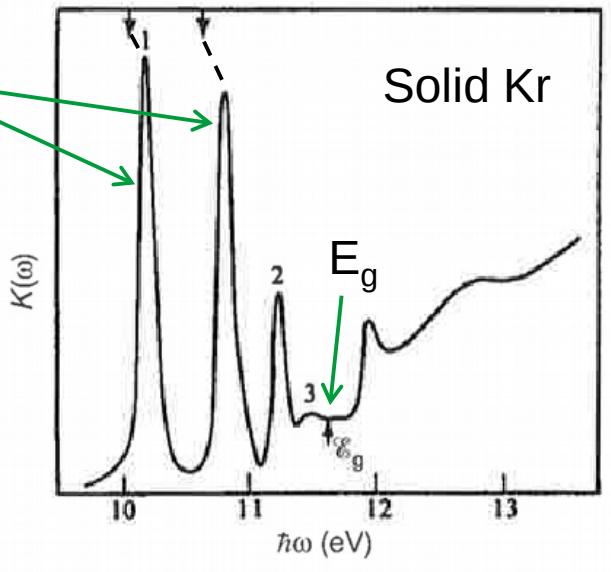


Optical Properties of Solids, Excitons (Elliott 5.8.3)

➔ Absorption of Electromagnetic Radiation in Insulators and Semiconductors:

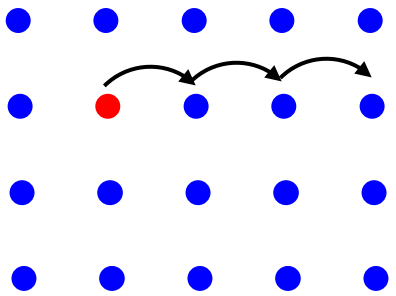


~Atomic $4p^6$ → $4p^5 5s$
spin-orbit splitting



A) Frenkel Exciton

-one excited atom in lattice ((core)hole + bound electron)
-excitation hops from atom to atom
-in good insulators: rare gas solids, alkali halides

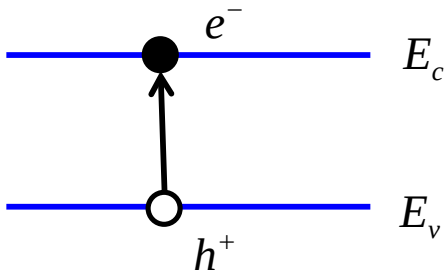


B) Mott-Wannier Exciton

Excitation, e^- and h^+, delocalized over several atoms

2-step formation:

1) e^- - h^+ excitation



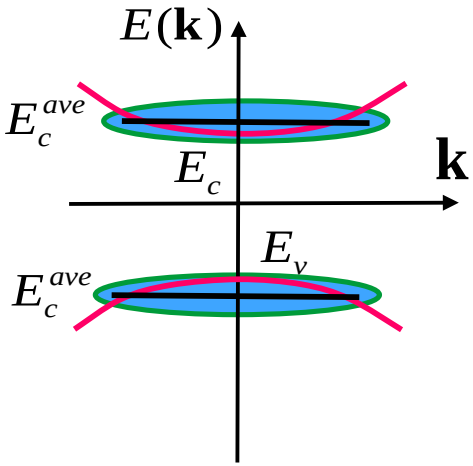
Potential

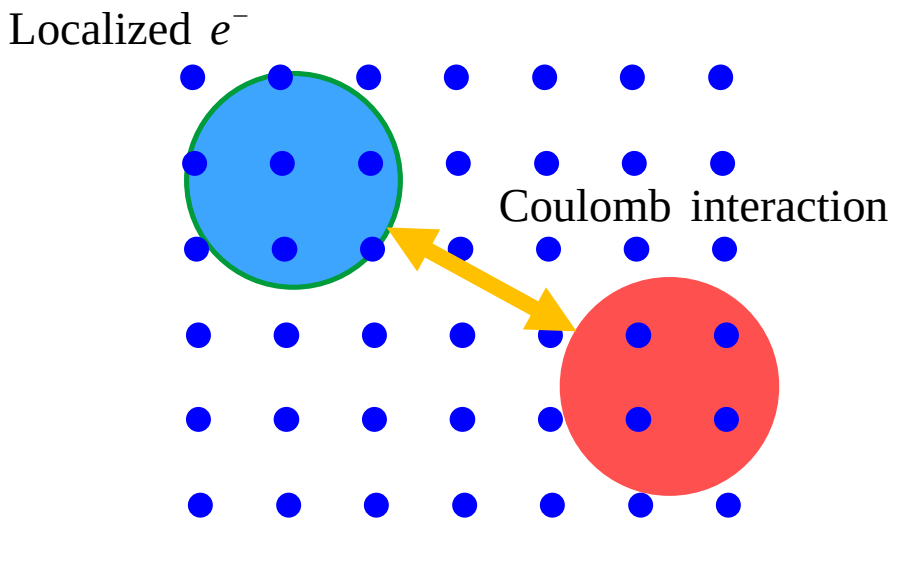
$$V^* = V^{\text{Ground state}}$$

Excitation energy

$$\Delta E = E_c - E_v$$

2) Formation of wave packets





$$\Delta E = E_c^{ave} - E_v^{ave} - V_{Coul}(e^-, h^+)$$

Lowest excited state in lattice

B) Mott-Wannier Exciton

H-atom model

Exciton total energy

H-atom ground state

Center of mass energy
(Zero-point energy in nanostructures)

$$\Delta E = E_c^{ave} - E_v^{ave} - \frac{13.6\,\mathrm{eV}}{(m_e/\mu^*)\varepsilon^2 n^2} + \frac{\hbar^2 K^2}{2\left(m_e^* + m_h^*\right)}$$

Scaling

Reduced effective band mass

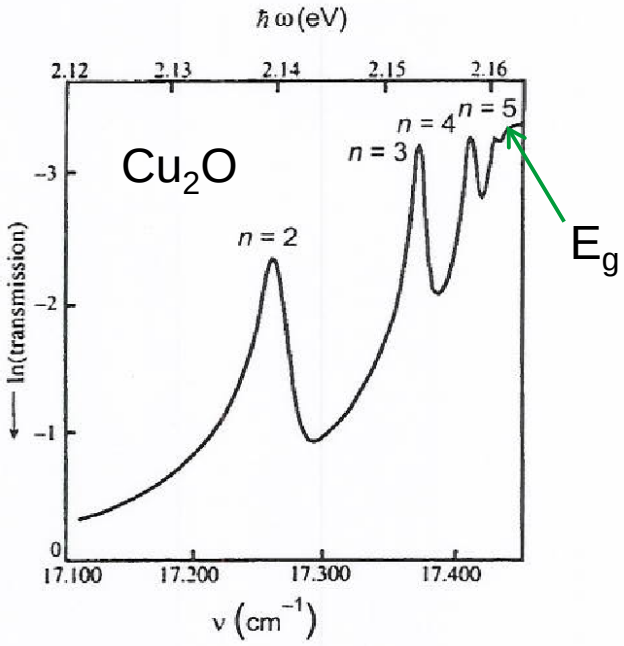
$$\frac{1}{\mu^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

Screening of Coulomb int.

$$\frac{-1}{4\pi\varepsilon_0 r} \rightarrow \frac{-1}{4\pi\varepsilon_0 \varepsilon r}$$

$$R^*/n^2$$

Effective Ryderg
Principal quantum number



p –like Rydberg series

Model valid if

$$a_{exc} = \frac{m_e}{\mu^*}\varepsilon a_0 >> a_0$$

~Localization ~Interatomic distance

Frenkel vs. Mott-Wannier Excitons

Larger band gap ➔ States are more localizd

➔ $\varepsilon \to 1, \quad m_e^*$ and m_h^* increase

➔ $a_{exc} = \dfrac{m_e}{\mu^*}\varepsilon a_0 \to a_0$

$R^* = \dfrac{13.6\,\text{eV}}{(m_e/\mu^*)\varepsilon^2}$ increases

➔ Mott-Wannier ➔ Frenkel excitons

Table 5.5 Exciton binding energies R^*

Mott–Wannier type		*Frenkel type*	
Material	R^* (meV)	*Material*	R^* (meV)
Si	14.7	BaO	56
Ge	4.2	KI	480
GaAs	4.9	KCl	400
GaP	3.5	KBr	400
InP	5.1	RbCl	440
CdS	29		
CdSe	15		
CdTe	11		

(After Burns (1985). Reproduced by permission of Academic Press, Inc.)

Optical Properties of Solids, Summary

(Dielectric Spectroscopy, Elliott 7.1.4)

Dielectric function $\varepsilon(\omega)$:

← Ionic motion, large μ_M ➔ low-ω region
← Electrons, small m_e ➔ low … high-ω region:
atomic polarizability, collective plasmon excitations (free electron gas),
damping (ε_2) by intra- and interband transitions

Damped harmonic oscillator

$$\mu\ddot{\mathbf{r}} + \gamma\mu\dot{\mathbf{r}} + k\mathbf{r} = q\mathbf{E}_{loc}(\omega)$$

➔ Frequency dependencies of different mechanisms
(Quantum mechanics may be needed, e.g., for atomic polarizability)

$$\tilde{\varepsilon}(\omega) = \varepsilon(\infty) + \sum_i \frac{f_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega}$$

ω_i = resonance frequency, *i* th mechanism
f_i = relative weighting (oscillator strength)
γ_i = damping constant (dissipation)

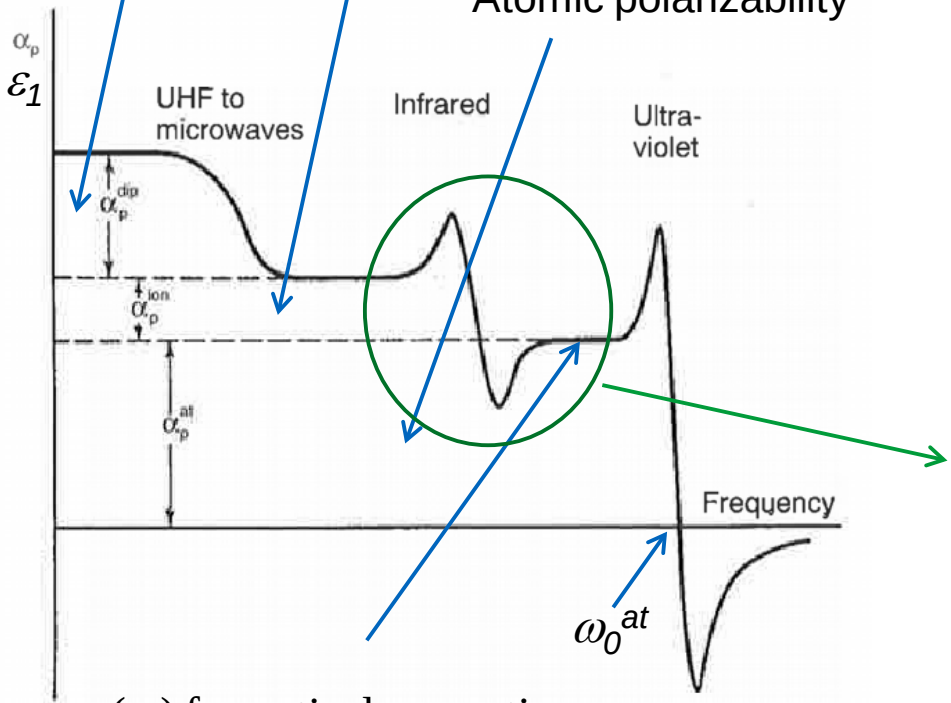
$$\varepsilon_1(\omega) = \varepsilon(\infty) + \sum_i \frac{f_i\left(\omega_i^2 - \omega^2\right)}{\left(\omega_i^2 - \omega^2\right)^2 + \gamma_i{}^2\omega^2} \quad ; \quad \varepsilon_2(\omega) = \sum_i \frac{f_i\gamma_i\omega}{\left(\omega_i^2 - \omega^2\right)^2 + \gamma_i{}^2\omega^2}$$

Optical Properties of Solids, Summary

Orientation of dipoles
(no resonance)

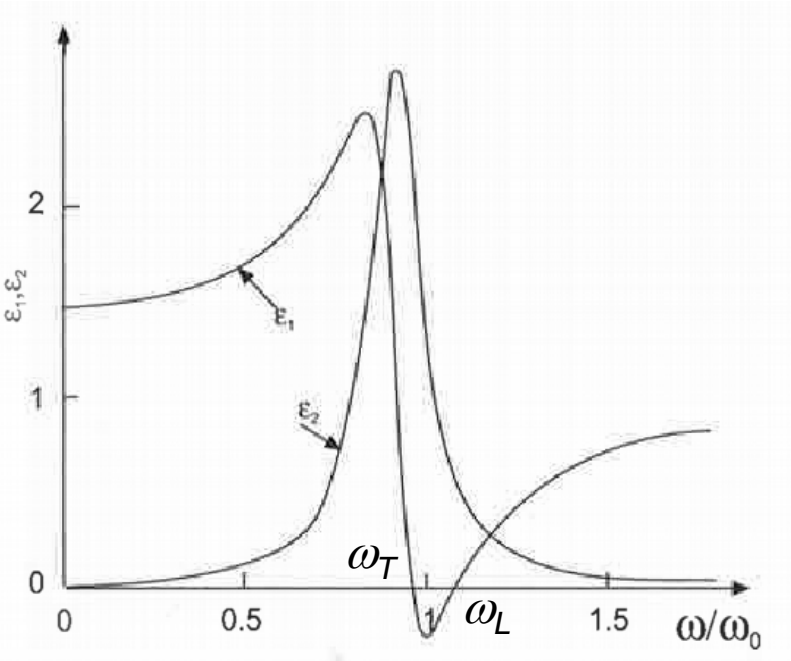
Ion movement

Atomic polarizability



$\varepsilon(\infty)$ for optical properties of ionic solids

Ionic solids,
Quenching different processes with increasing frequency



Light-Material Interaction, Macroscopic Maxwell's Equations

Harmonic (**k,** ω) fields

$\mathbf{E},\ \mathbf{D},\ \mathbf{B},\ \mathbf{H}$

Material parameters

$\varepsilon(\omega),\ \sigma(\omega)$

$\mathbf{D} = \varepsilon_0 \varepsilon(\omega)\mathbf{E}$

$\mathbf{j} = \sigma(\omega)\mathbf{E}$

Faraday

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

Ampere-Maxwell

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \mu_0 \frac{\partial \mathbf{D}}{\partial t}$$

Dispersion relation

$$k^2 = \frac{\omega^2 \varepsilon(\omega)}{c^2}$$

- Propagation or reflection of EM radiation at the vacuum-matter interface
- Coupled propagating radiation-matter modes, polaritons in ionic solids

Refractive index

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

Intensity decay

$$I \propto E_0^2 \exp\left[-\frac{2\omega\kappa_i}{c} x\right]$$

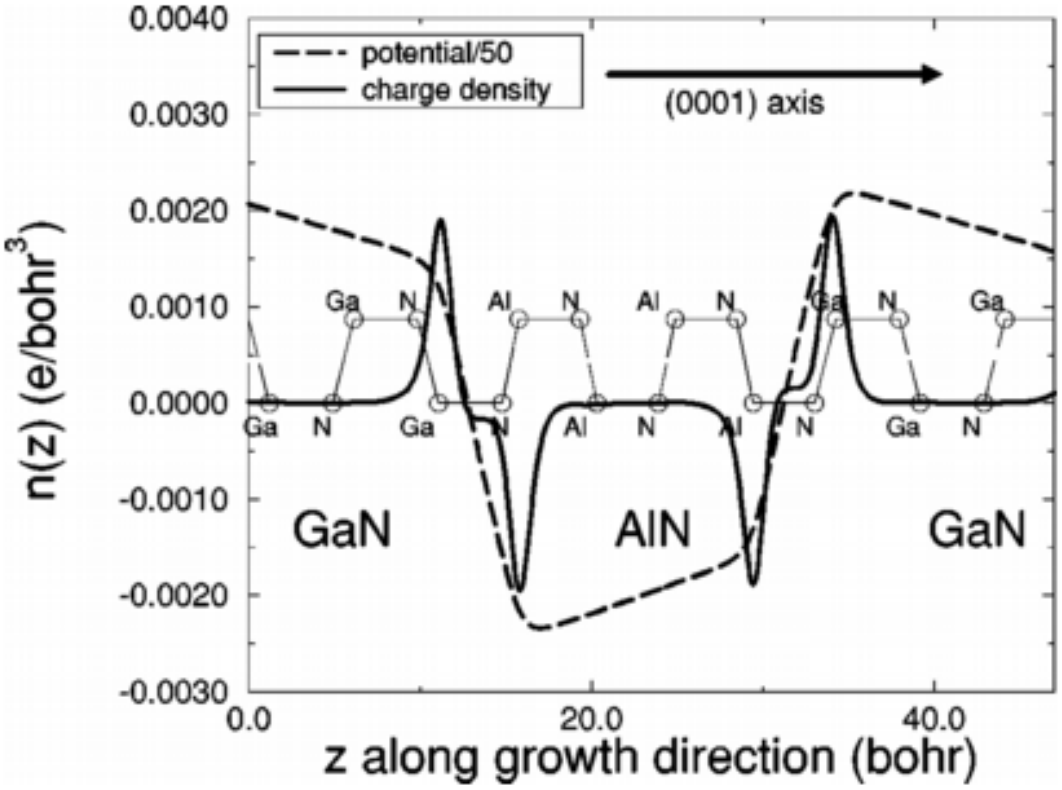
Reflectivity

$$R = \frac{(n_r - 1)^2 + \kappa_i^2}{(n_r + 1)^2 + \kappa_i^2}$$

Lecture Assignment

Heterostructures of polarized materials

GaN and AlN have (non-cubic) wurtzite structure ➔ spontaneus polarization in c (or (0001)) –direction ➔ internal electric fields



Charge density and potential averaged over planes parallel to the interface.

F. Bernardini and V. Fiorentini, PRB, **57**, R9427 (1998).

Spontaneous Polarization

Polarization is a ill-defined bulk property

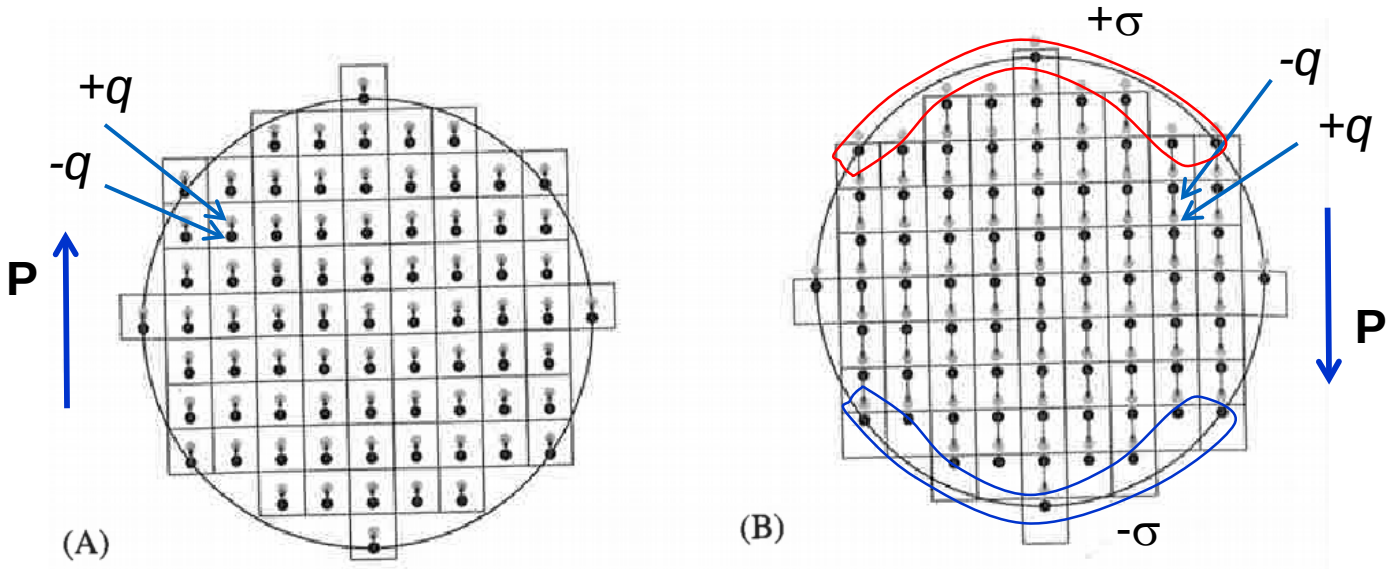


Figure 22.1. When charges are distributed throughout a solid, the polarization density depends upon how they are grouped. In (A), positive and negative charges have been grouped with their nearest neighbors. In (B), they have been grouped so that the polarization now points in the opposite direction. In compensation, there is now a substantial surface charge.

M.P. Marder, Condensed Matter Physics

Surface charge is important - But polarization should be a bulk property?

Changes in polarization can be measured and are sufficient

➔ Solution of the dilemma

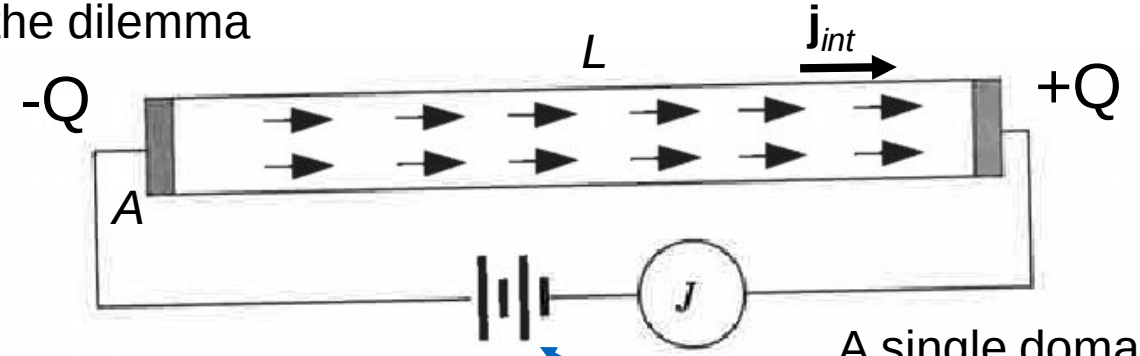


Figure 22.2. The spontaneous electric polarization of a sample is measured by cooling it below the ferroelectric transition temperature in an electric field, and then measuring the total charge that flows between the ends.

M.P. Marder, Condensed Matter Physics

Polarization

$$|\mathbf{P}| = QL/V = Q/A = \left| \int^{t} dt' \, \mathbf{j}_{\text{int}}(t') \right|$$

Absolute values of **P** are actually not needed!

Berry's phase formalism (1984) (based on electron system wavefunction)

P, e.g., from first – principles calculations

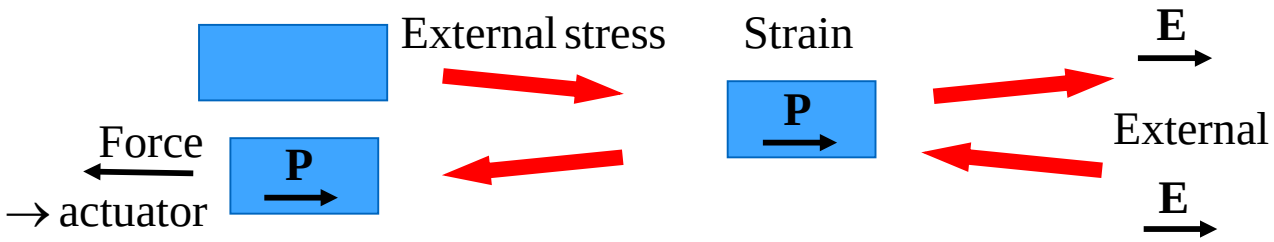
Distinguishing between metals and insulators

Reviews: R. Resta J. Phys.: Condens. Matter **14**, R625 (2002), N. Spaldin, J. of Solid State Chemistry **195**, 2 (2012).

Spontaneous Polarization

(Elliott 7.1.5)

Piezoelectric materials



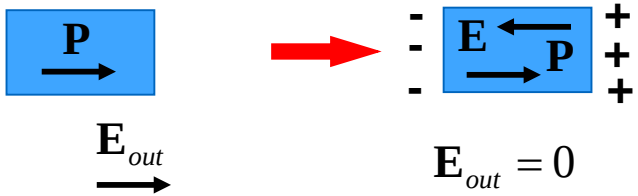
Subset: Pyroelectric materials

High temperature ("burning")

$\mathbf{P} = 0$

Cooling → phase transition

with uniaxial contraction or expansion



$\mathbf{E}_{out}$

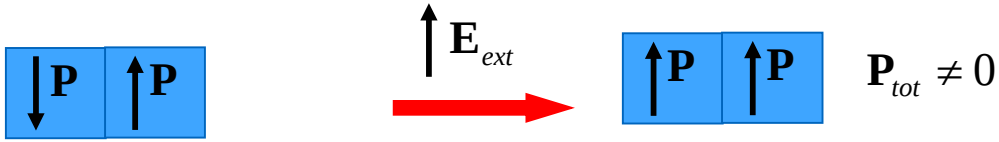
Accumalation of counterions

$\Rightarrow \mathbf{E}$ inside $\Rightarrow \mathbf{E}_{out} \rightarrow 0$

$\mathbf{E}_{out} = 0$

Subsubset: Ferroelectric materials

Domain structure with $\mathbf{P}_{tot} = 0$



Ferroelectricity, example $BaTiO_3$

Elliott 7.1.5

Perovskite structure

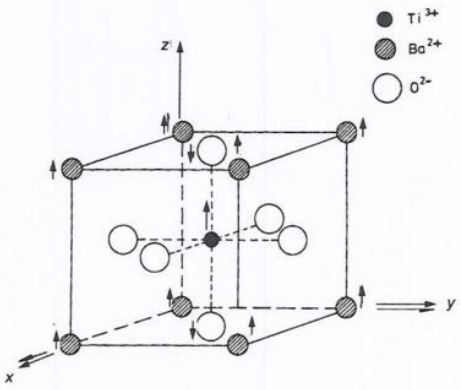


Fig. 7.13 The cubic perovskite (non-pyroelectric) structure of $BaTiO_3$ stable above 134 °C. The arrows show the relative magnitude and direction of the atomic displacements in the transition to the pyroelectric tetragonal phase stable between -5 and 134 °C. The oxygen atoms have been taken to be fixed (see also Fig. 7.19a).

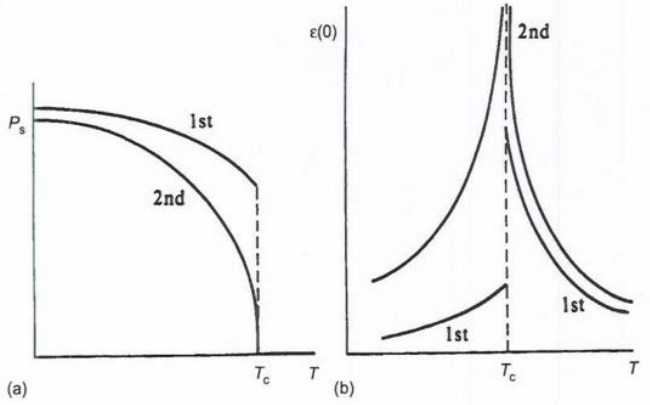
Phase transitions

First-order: - Discontinuous **P**

- Discontinuous $\varepsilon(0)$

Second-order: - Continuous **P**

- Divergent $\varepsilon(0)$



$T > 134^{\circ}\mathrm{C}$

Paraelectric (non-ferroelectric) cubic structure

$-5^{\circ}\mathrm{C} < T < 134^{\circ}\mathrm{C}$

Tetragonal structure with + ions moving ↑, - ions ↓

P

Ferroelectric

$T = 134^{\circ}\mathrm{C}$ = Ferroelectric Curie-temperature

First-order phase transition

(Cf. Metal-organic perovskite solar cells)

Spontaneous Polarization

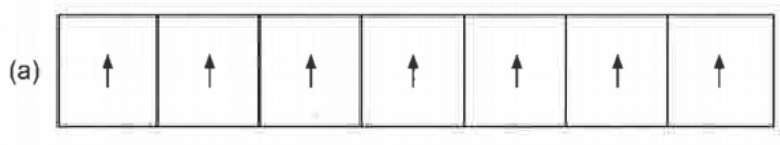
Elliott 7.1.5

Domain Structures and Hysteresis of Polarization

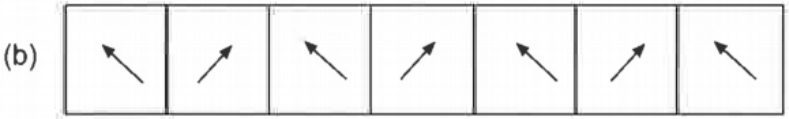
Movement of domain walls

→ Hysteresis

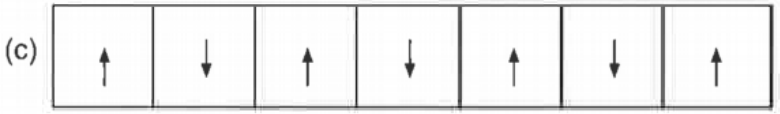
Ferroelectric

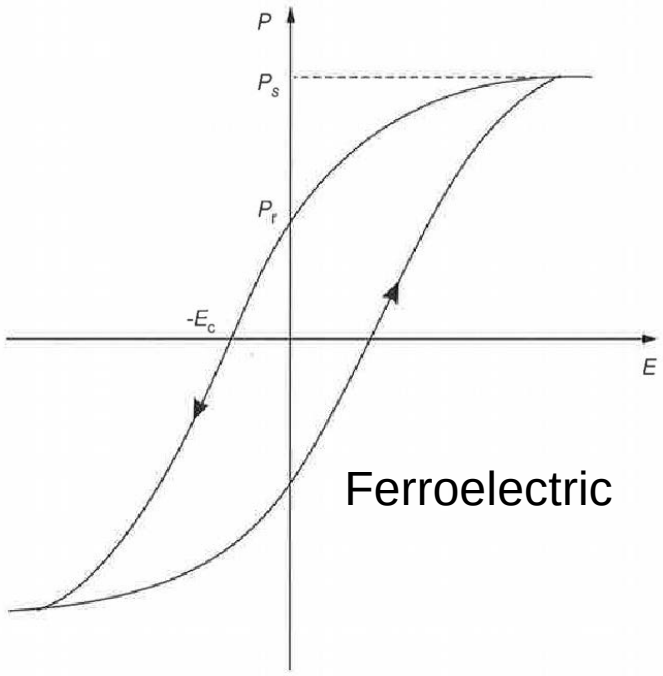


Ferrielectric



Anti-ferrielectric





Magnetic properties of materials

- Response of materials to an external magnetic field
  - Magnetic quantities, magnetism is quantum mechanics (home work)
  - Quantum mechanical description
  - Atomic diamagnetism, paramagnetism
  - Response of free electron gas

TODAY

Models for materials' magnetic properties and phenomena

- Spontaneous magnetism Ferromagnetism and antiferromagnetism
  - Exchange interaction, H_2 molecule, Heisenberg spin Hamiltonian
  - Mean-field approximation for ferromagnetism of magnetic moments
  - Spin waves (low-energy excitations)
  - Free electron gas
  - Stoner model for ferromagnetism of itinerant electrons
  - Antiferromagnetism
  - Domain structure

Magnetic properties of materials, Literature

- Griffiths Ch. 6 (Classical field theory) (Mycourses)
- Bolton-Freake (Eds.) Quantum mechanics of matter Chs. 5, 2, 1 (ebook)

- Elliott Ch. 7.2
- Ashcroft-Mermin, Chs. 31, (32), 33, App. P (Mycourses)
- Ibach-Lüth, Ch. 8
- Simon, Oxford solid state basics, Chs. 19-23: a short presentation (ebook)

Magnetic properties of materials

➔ Technology (engines, transformers, actuators, levitation, memory devices, antennas, electronics …)

🡐 Novel materials: (neo magnets), dilute magnetic semiconductors, multiferroic materials for spintronics, magnetic nanoparticles

➔ Theory: Electrons in solids, (nuclei)

single-electron band theory ←→ many interacting electrons

local effects ←→ collective effects

Magnetic quantities

(Elliott 7.2.1)

Magnetic dipole moment of a current on a loop

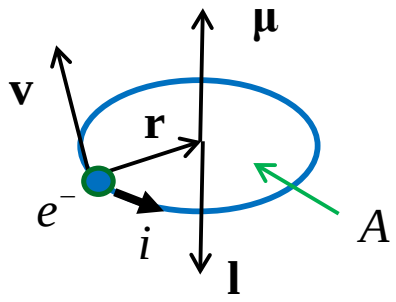
$\boldsymbol{\mu} = iA\hat{\mathbf{n}}$ $\quad [\boldsymbol{\mu}] = 1\,\mathrm{Am}^2$

[E(7.78)]

Orbital angular momentum

$$|\boldsymbol{\mu}| = \frac{|-e|v}{2\pi r}\pi r^2 = \frac{|-e|}{2m_e}|\mathbf{r}\times\mathbf{p}| = \frac{|-e|}{2m_e}|\mathbf{l}| \quad \Rightarrow \quad \boldsymbol{\mu} = \frac{-e}{2m_e}\mathbf{l}$$

Electron on a circular path around a nucleus



Quantum Mechanics

Expectation value in $\hbar$

$$\Rightarrow \quad \mu_z = -\mu_B \langle \hat{\mathbf{l}}_z \rangle$$

$$\mu_B = \frac{e\hbar}{2m_e}$$ Bohr magneton

Spin $\Rightarrow$ $\mu_z = -\mu_B g_0 < \hat{\mathbf{s}}_z >$ $\quad < \hat{\mathbf{s}}_z >= \pm 1/2$

$g_0 \approx 2$ Gyromagnetic ratio

Many electrons in atom

Landé factor

$$\mu_z = -\mu_B \langle \hat{\mathbf{L}}_z + 2\hat{\mathbf{S}}_z \rangle = -\mu_B g \langle \hat{\mathbf{J}}_z \rangle$$

Total orbital and total spin angular momenta of all electrons

Total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

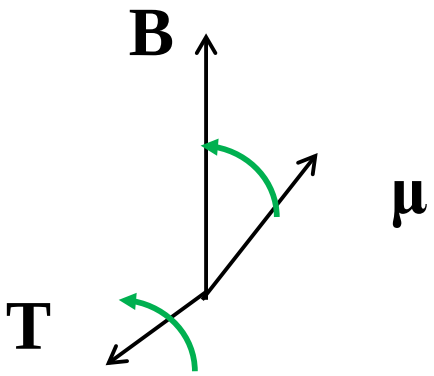
Magnetic quantities

(Elliott 7.2.1)

(Classical physics)

Magnetic flux density

Torque on magn. moment $\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B}$ [E(7.80)] → $\mathbf{B}$ $[\mathbf{B}] = 1\,\mathrm{T}$



Magnetic field strength

External applied field $\mathbf{B}_0 = \mu_0 \mathbf{H}$ $[\mathbf{H}] = 1\ \mathrm{A/m}$

μ_0: Vacuum permeability (SI system)

Magnetization = Magnetic moment / volume

[E(7.79)] $\mathbf{M} = \sum_i \boldsymbol{\mu}_i / V$ $[\mathbf{M}] = 1\,\mathrm{A/m}$

Total magnetic flux density

$\mathbf{B} = \mathbf{B}_0 + \mu_0 \mathbf{M}$ → $\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})$ [E(7.81)]

(Cf. homework)

Magnetic quantities

(Elliott 7.2.1)

Magnetic susceptibility (Material property)

$$\mathbf{M} = \chi_m \mathbf{H}$$

$$\mu_0 \mathbf{M} = \chi_m \mathbf{B}_0$$

[E(7.83)]

$$\chi_m = \frac{\partial M}{\partial H} = \mu_0 \frac{\partial M}{\partial B_0}$$

Paramagnetic material

$$\chi_{m,p} > 0$$

$$\chi_{m,d} < 0$$

Diamagnetic material

Relative permeability

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu_r \mu_0 \mathbf{H}$$

(cf. $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon \mathbf{E}$)

[E(7.82)]

$$\mu_r = 1 + \chi_m$$

E(7.84)]

For dia- and paramagnets

$$\chi_m << 1$$

$$\mu_r \approx 1$$

$$\mathbf{B}_{loc} \approx \mathbf{B}_0$$

Magnetization vs. thermodynamics

(AM Eqs. (31.1)-(31.8))

$$\mathbf{M} = \sum_i \boldsymbol{\mu}_i / V$$

Energy of moment *i* in field $\mathbf{B}_0$

$$\Delta E_i = -\boldsymbol{\mu}_i \bullet \mathbf{B}_0$$

(Classical $\boldsymbol{\mu}_i$)

Homogeneous system of moments at T=0 in field $\mathbf{B}_0$

Total energy

$$E_0 = \sum_i -\boldsymbol{\mu}_i \bullet \mathbf{B}_0 = -V\mathbf{M}_0 \bullet \mathbf{B}_0$$

$$M_0(B_0) = -\frac{1}{V}\frac{\partial E_0}{\partial B_0}$$

$\mathbf{M}_0 \parallel \mathbf{B}_0$

T>0, Several excited states *n*

$$E_n = \sum_i -\boldsymbol{\mu}_i^{\,n} \bullet \mathbf{B}_0 = -V\mathbf{M}_n \bullet \mathbf{B}_0$$

Maxwell-Botzmann statistics

$$M(B_0) = \frac{\sum_n M_n \exp(-E_n / k_B T)}{\sum_n \exp(-E_n / k_B T)}$$

$\mathbf{M}_n \parallel \mathbf{B}_0$

Partition function

$$Z(T) = \sum_n \exp\left[-E_n(\mathbf{B}_0)/k_B T\right]$$

Helmholtz free energy

$$F_H (= U - TS) = -k_B T \ln Z$$

$$M = -\frac{1}{V}\frac{\partial F_H}{\partial B_0}$$ [E(7.74)]

$$\mathbf{M} = \chi_m \mathbf{H} = \chi_m \mathbf{B}_0 / \mu_0$$

$$\chi_m = \mu_0 \frac{\partial M}{\partial B_0} = -\frac{\mu_0}{V}\frac{\partial^2 F_H}{\partial B_0^2}$$

Magnetism is a quantum phenomenon

Bohr – van Leeuwen theorem: Classical interacting system is insensitive to the magnetic field **B**.

Proof.

$$M = -\frac{1}{V}\frac{\partial F_H}{\partial B_0}$$

$$F_H = -k_B T \ln Z$$

$$Z(T) = \sum_n \exp\left[-E_n(\mathbf{B_0})/k_B T\right]$$

Classical mechanics

$$Z(T) \propto \iint \exp\left[-H(\mathbf{p},\mathbf{r})/k_B T\right] d\mathbf{p}\, d\mathbf{r}$$

Minimal substitution

$$\mathbf{p} = m_e \mathbf{v} - e\mathbf{A}$$

[E(7.76)]

Vector potential

$$\mathbf{B} = \nabla \times \mathbf{A}$$

Hamiltonian function

$$H(\mathbf{p},\mathbf{r}) = \frac{1}{2m_e}\left(\mathbf{p} + e\mathbf{A}\right)^2 + V(\mathbf{r})$$

[E(7.77)]

$\mathbf{p}$ - integral over an ∞ p - volume

$e\mathbf{A}$ finite shift of origin in integral

$$Z \neq Z(\mathbf{A}) \quad \text{or} \quad Z(\mathbf{B_0})$$

$$\mathbf{M} = 0$$

Magnetic properties

- Response of materials to an external magnetic field
  - Magnetic quantities, magnetism is quantum mechanics (home work)
  - Quantum mechanical description
  - Atomic diamagnetism, paramagnetism (lecture work)
  - Response of free electron gas

The next lecture

- Spontaneous magnetism Ferromagnetism and antiferromagnetism
  - Exchange interaction, H_2 molecule, Heisenberg spin Hamiltonian
  - Mean-field approximation for ferromagnetism of magnetic moments
  - Spin waves (low-energy excitations)
  - Free electron gas
  - Stoner model for ferromagnetism of itinerant electrons
  - Antiferromagnetism
  - Domain structure