

Course review

## I. Crystal structure, and symmetry

- ❖ Crystal: atoms are arranged so that their positions are periodic in all three dimensions. Crystal lattice - the periodic array of points.  
An atom or a group of atoms associated with every lattice point is called *basis* of the lattice
- ❖ In addition to periodicity, each lattice can have other symmetry properties (inversion, mirror planes, rotation axes)
- ❖ 7 crystal systems and 14 Bravais lattices
- ❖ A particular combination of symmetry operations determined by symmetry of the basis and the symmetry of the Bravais lattice defines a point symmetry group. There are 32 point groups - crystal classes.
- ❖ Notation for crystallographic directions and planes: Miller indices

## II. Interatomic forces and types of chemical bonds

- ❖ Attractive electrostatic interaction between electrons and nuclei – the force responsible for cohesion of solids
- ❖ Repulsive interaction between atoms is primarily due to electrostatic repulsion of overlapping charge distributions and Pauli principle
- ❖ Several types of attractive forces:
  - Ionic crystals – electrostatic forces between "+" and "-" ions
  - Covalent bond: overlap of charge distributions with antiparallel spin
  - Metals: reduction of kinetic energy of electrons in free state compared to the localized state of a single atom
  - Secondary forces (Van der Waals, hydrogen) become significant when the other bonds are impossible, e.g. in inert gases
- ❖ Physical properties are closely related to the type of bonding

## Diffraction of waves by crystal lattice

- ❖ Most methods for determining the atomic structure of crystals are based on scattering of particles/radiation (X-rays, electrons, neutrons). The wavelength of the radiation should be comparable to a typical interatomic distance (few Å=10<sup>-8</sup> cm)
- ❖ The Bragg law: condition for a sharp peak in the intensity of the scattered radiation. Various statements of the Bragg condition:  
$$2d \cdot \sin\theta = m\lambda ; \quad \Delta\mathbf{k} = \mathbf{G} ; \quad 2\mathbf{k} \cdot \mathbf{G} = G^2$$
- ❖ Constricting the reciprocal lattice from the direct lattice. Reciprocal lattice is defined by primitive vectors:  
$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3, \quad \mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1, \quad \mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$
- ❖ A reciprocal lattice vector has the form  $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$   
It is normal to (hkl) planes of direct lattice
- ❖ The set of reciprocal lattice vectors determines the possible scattering wave vectors for diffraction

## Diffraction, reciprocal lattices and Brillouin zones

- ❖ First Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice
- ❖ Only waves whose wave vector drawn from the origin terminates on a surface of the Brillouin zone can be diffracted by the crystal
- ❖ Reciprocal lattices for common structures (e.g. sc ↔ sc; bcc ↔ fcc) Brillouin zones for these common structures
- ❖ Diffraction amplitude is determined by a product of several factors: atomic form factor, structural factor, Debye-Waller factor

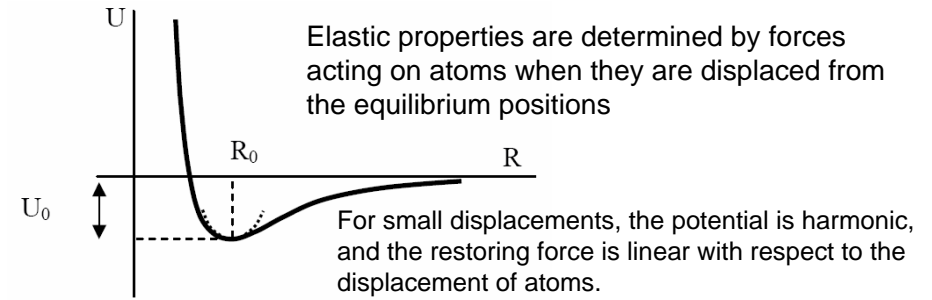
- Atomic scattering factor (form factor) reflects distribution of electronic cloud.

- Structure factor – for lattices with a basis of several atoms

$$F = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)}$$

- Debye-Waller factor – atomic vibrations are taken into account

## Elastic properties



Elastic properties are described by considering a crystal as a homogeneous continuum medium rather than a periodic array of atoms

• Applied forces are described in terms of *stress*  $\sigma$ ,

• Displacements of atoms are described in terms of *strain*  $\varepsilon$ .

• Elastic constants  $C$  relate stress  $\sigma$  and strain  $\varepsilon$ , so that  $\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}$   
(Hooke's law)

## Lattice vibrations

❖ Elastic waves  $\frac{\partial^2 u}{\partial t^2} = \frac{C_{eff}}{\rho} \frac{\partial^2 u_x}{\partial x^2}$  sound velocity  $v = \sqrt{\frac{C_{eff}}{\rho}}$

❖ All crystal vibrational waves can be described by wave vectors within the first Brillouin zone in reciprocal space

❖ More than one atom in a unit cell – acoustic and optical vibrations.

In general three-dimensional lattice with  $s$  atoms per unit cell there are  $3s$  vibrational branches: 3 acoustic,  $3s - 3$  optical

❖ Phonon - the quantum of lattice vibration.  
Energy  $\hbar\omega$ ; momentum  $\hbar\mathbf{q}$

❖ Density of states is important characteristic of lattice vibrations;  
It is related to the dispersion  $\omega = \omega(q)$ .

Simplest case of isotropic solid, for one branch:  $D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}$

Real density of vibrational states is more complicated

## Phonon heat capacity, thermal conductivity, anharmonism

❖ Heat capacity is related to the density of states.

❖ Debye model – good when acoustic phonon contribution dominates.

At low temperatures gives  $C_v \propto T^3$

❖ Einstein model - simple model for optical phonons  
( $\omega(q) = \text{constant}$ , DOS is approximated by a  $\delta$ -function)

❖ At high  $T$  both models lead to the Dulong-Petit law:  $C_v = 3Nk_B$

❖ Phonon thermal conductivity  $K = \frac{1}{3} C_v l$

❖ Anharmonism of potential energy is responsible for such effects as:

- phonon-phonon interaction
- thermal expansion
- Pressure and temperature dependence of elastic constants

## Free electron model of metals

❖ Free electron model – simplest way to describe electronic properties of metals: the valence electrons of free atoms become conduction electrons in crystal and move freely throughout the crystal.

❖ Fermi energy - the energy of the highest occupied electronic level at  $T = 0$  K;

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \quad k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3} \quad v_F = \frac{\hbar}{m} \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

❖ Density of states of 3D free electron gas:

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} = \frac{3N}{2E}$$

❖ Electrical conductivity:

$$\sigma = -\frac{ne^2\tau}{m^*}$$

$$\rho = \rho_i + \rho_{ph}(T)$$

❖ Heat capacity of free electron gas at low temperatures  $k_B T \ll E_F$ :

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

❖ Thermal conductivity: Wiedemann-Franz law

$$K = L\sigma T \quad L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2$$

## Limitations of free electron model

The free electron model gives a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity. However, it fails to explain a number of important properties and experimental facts, for example:

- the difference between metals, semiconductors and insulators
- It does not explain the occurrence of positive values of the Hall coefficient.
- Also the relation between conduction electrons in the metal and the number of valence electrons in free atoms is not always correct. Bivalent and trivalent metals are consistently less conductive than the monovalent metals (Cu, Ag, Au)

⇒ need a more accurate theory, which would be able to answer these questions – the band theory

## Band theory

❖ The Bloch theorem: the wave function for an electron in periodic potential can be written in the form:  $\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$  where

$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$  - a periodic function with the period of the lattice

❖ The energy spectrum of electrons consists of a set of continuous *energy bands*, separated by regions with no allowed states - *gaps*

❖ Function  $E(\mathbf{k})$  satisfies the symmetry properties of a crystal, in particular, the translational invariance:  $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$

This allows considering the first Brillouin zone only.

Also, inversion symmetry:  $E(\mathbf{k}) = E(-\mathbf{k})$

❖ Nearly free electron model – weak crystal potential. Electron behaves essentially as a free particle, except the wave vectors close to the boundaries of the zone. In these regions, energy gaps appear.

❖ Tight binding model – strong crystal potential, weak overlap. The band width increases and electrons become more mobile (smaller effective mass) as the overlap between atomic wave functions increases

❖ Concept of effective mass: in a periodic potential electron moves as in free space, but with different mass:

$$\left( \frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \quad i, j = x, y, z$$

❖ Physical origin of effective mass: crystal field

❖ Metals: partially filled bands; insulators – at 0 K the valence band is full, conduction band is empty. Semiconductors and semimetals.

❖ Perfectly periodic lattice – no scattering of electrons - velocity remains constant

- ❖ Density of states - number of electronic states per unit energy range. Simple case:

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

- ❖ Concept of the hole: consider transport of the holes for the bands, which are nearly occupied.

- ❖ Electrical conductivity:

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau_F D(\varepsilon_F)$$

- ❖ Cyclotron frequency:

$$\omega_c = \frac{eB}{m^*}$$

- ❖ Hall coefficient for metals with both electrons and holes:

$$R = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2}$$

## Semiconductors

- ❖ Semiconductors are mostly covalent crystals with moderate energy gap (~0.5 – 2.5 eV)

- ❖ Intrinsic carrier concentration

$$n = 2 \left( \frac{k_B T}{2\pi \hbar^2} \right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2k_B T} = p = n_i$$

- ❖ Fermi level position in intrinsic semiconductor:

$$\mu = \frac{E_v + E_c}{2} + \frac{3}{4} k_B T \ln \frac{m_h}{m_e}$$

- ❖ In a doped semiconductor, many impurities form shallow hydrogen-like levels close to the conductive band (donors) or valence band (acceptors), which are completely ionized at room T:

$$n = N_d \quad p = \frac{n_i^2}{N_d} \quad \text{or} \quad p = N_a \quad n = \frac{n_i^2}{N_a}$$

In the Bohr model, the binding energy is  $E_d = -\frac{e^4 m_e}{2\varepsilon^2 \hbar^2}$

## Semiconductors

- ❖ Conductivity of semiconductors:  $\sigma = ne\mu_e + pe\mu_h$

$$\text{mobility: } \mu_e = \frac{e\tau_e}{m_e}$$

- ❖ Cyclotron resonance is used to obtain information on effective masses.

- ❖ Hall coefficient:  $R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(n\mu_e + p\mu_h)^2}$

Hall measurements are used to determine carrier concentration and mobility.

- ❖ In high electric field, the carriers acquire significant energy and become "hot". This affects mobility and can cause current instabilities (e.g. Gunn effect caused by negative differential conductivity due to inter-valley transfer)

- ❖ Mechanisms of optical absorption and luminescence (band-to-band, excitonic, free carrier, impurity-related).

Fundamental absorption occurs above the bandgap.

- ❖ photoconductivity – increase of conductivity by generation of additional carriers by electromagnetic radiation

- ❖ Diffusion. Basic relations are Fick's law and the Einstein relation  $D_n = \frac{\mu_n k_B T}{e}$

## Basic physical principles of some semiconductor devices

- ❖ *p-n* junction: both electrons and holes diffuse across the junction – potential barrier develops, called *built in voltage*  $V_{bi}$ :

$$V_{bi} = kT \ln \frac{N_A N_D}{n_i^2}$$

- ❖ The junction acts as rectifier. The current vs applied voltage  $V$  is

$$I = I_0 (e^{eV/kT} - 1) \quad \text{Forward: } I \approx I_0 e^{eV/kT} \quad \text{Reverse: } I \approx -I_0$$

$$j_0 = e \left( \frac{D_n n_{p0}}{L_n} + \frac{D_p p_{n0}}{L_p} \right) \quad \text{or} \quad j_0 = en_i^2 \left( \frac{D_n}{L_n p_{p0}} + \frac{D_p}{L_p n_{n0}} \right)$$

- ❖ Bipolar junction transistor – two back to back junctions: emitter is forward biased, collector is reverse biased

Works as amplifier: when a signal is applied at the emitter, a current pulse passes through the base-collector circuit. The voltage gain is:

$$\frac{dV_l}{dV_e} = \frac{dV_l}{dI_e} \frac{dI_e}{dV_e} = \frac{\alpha R_l I_e}{kT/e}$$

- ❖ Tunnel diode is realized when the doping levels in a *p-n* junction are very high, so the junction width is very small – tunneling occur.

## Dielectric properties of solids

- ❖ The dielectric constant is defined by the equation:  $\mathbf{D} = \epsilon \mathbf{E}$ , where  $\mathbf{D}$  is the electric displacement,  $\mathbf{E}$  – average field inside dielectric.

$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$ , where polarization  $\mathbf{P} = N\mathbf{p}$  - dipole moment per unit volume

- ❖ Polarizability  $\alpha$  is defined via  $\mathbf{p} = \alpha \mathbf{E}$ ;  $\Rightarrow$  polarization  $\mathbf{P} = \epsilon_0 \chi \mathbf{E}$ , where  $\chi = N\alpha/\epsilon_0$  – electric susceptibility. Generally,  $\chi$  is a tensor

- ❖ Local field correction (for cubic crystals) :  $\mathbf{E}_{loc} = \mathbf{E} + \frac{1}{3\epsilon_0} \mathbf{P}$

leads to the Clausius-Mossotti relation:  $\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}$

- ❖ In general, molecular polarizability is the sum of the electronic, ionic, and dipolar contributions:  $\alpha = \alpha_e + \alpha_i + \alpha_d$

- ❖ Ionic contribution to dielectric function is related to lattice vibrations and exhibits dispersion in infrared region, given by the Lyddane-Sachs-Teller relation:

$$\epsilon(\omega) = \epsilon_\infty \prod_j \frac{\omega_{LOj}^2 - \omega^2}{\omega_{TOj}^2 - \omega^2}$$

- ❖ Electronic polarizability is given by

$$\alpha(\omega) = \frac{e^2}{m} \left( \underbrace{\frac{1}{-\omega^2 + i\omega\gamma_e}}_{\text{free electrons}} + \sum_j \underbrace{\frac{f_j}{\omega_{0j}^2 - \omega^2 + i\omega\gamma_j}}_{\text{bound electrons}} \right) \quad n^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_e}}$$

- ❖ Dielectric function and refractive index are generally complex:  $\epsilon_r = \epsilon_r' + i\epsilon_r''$ ;  $\tilde{n} = n_R + in_I$ ;  $\epsilon_r' = n_R^2 - n_I^2$ ;  $\epsilon_r'' = 2n_R n_I$   
absorption coefficient  $\alpha = 2k_0 n_I$   $n_I$  - extinction coefficient

## Magnetic properties of materials

- ❖ When a material medium is placed in a magnetic field, the medium is magnetized. Magnetisation is proportional to the magnetic field:

$\mathbf{M} = \chi \mathbf{H}$ ;  $\chi$  - magnetic susceptibility of the medium  
magnetic permeability  $\mu = \mu_0(1 + \chi)$ ;  $\mu_r = 1 + \chi$

- ❖ Langevin diamagnetism - ions or atoms with all electronic shells filled  
negative magnetic susceptibility:  $\chi = -\frac{\mu_0 e^2 N Z \langle r^2 \rangle}{6m}$

- ❖ Langevin paramagnetism: if an atom has moment  $\mu$ , then classical paramagnetic susceptibility  $\chi = \frac{\mu_0 N \mu^2}{3k_B T}$

quantum treatment  $\rightarrow$  same result for  $\mu = g[J(J+1)]^{1/2} \mu_B$   $\mu_B = \frac{e\hbar}{2m}$

- ❖ In metals, conduction electrons make a spin paramagnetic contribution:  $\chi = \mu_B^2 D(E_F)$  - independent on T

- ❖ Conduction electrons also exhibit diamagnetism due to the cyclotron motion, which is equal to 1/3 of the spin paramagnetic contribution.

- ❖ Ion core effect must also be taken into account

- ❖ Ferromagnetic material exhibits spontaneous magnetization below the Curie temperature ( $T_C$ ).

Above the  $T_C$  – paramagnetic; Curie-Weiss Law:

- ❖ Cause for ferromagnetism: - exchange interaction

- ❖ Due to the exchange interaction, a spin disturbances propagates through a material as a spin waves. Their quanta - magnons

- ❖ When a magnetic field is applied to a material, the dipole moments of the atoms precess around it with a frequency  $\omega_0 = \gamma B_0$ ;  
 $\gamma = ge/2m$  – gyromagnetic ratio.

When an electromagnetic wave of frequency  $\omega = \omega_0$  passes through material, it is absorbed by the dipoles. This is called electron paramagnetic resonance

Nuclear magnetic resonance – the same phenomenon caused by nuclear magnetic moments