

## Free Electrons in a Metal

- in a typical metal each atom contributes **one** electron to the delocalized **electron gas** describing the conduction electrons
- if these electrons would behave like an ideal gas each one would contribute  $\frac{3}{2} kT$  to the total energy of the solid

$$E_e = N_0 \frac{3}{2} kT$$

- thus the electronic specific heat would be

$$C_{V_e} = \left( \frac{\partial E_e}{\partial T} \right)_V = \frac{3}{2} R$$

- how come that the specific heat of a solid at high temperatures is well described by the Dulong Petit law independently of whether the solid is a metal or an insulator
- resolution: electrons are fermions and obey the Fermi-Dirac statistics (instead of the Bose-Einstein statistics of phonons or any other harmonic oscillators)
- in the high temperature limit both phonons and electrons obey Maxwell-Boltzmann statistics
- BUT the high temperature limits could occur at different temperatures for electrons and phonons

phys4.16 Page 1

## Average Occupancy per Electron State

- is given by the Fermi-Dirac distribution

$$f_{FD} = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1}$$

- to find the number of electrons  $n(\epsilon)$  at a certain energy in a metal we need to determine the number of available states  $g(\epsilon)$
- consider free non-interacting electrons in a box described by 'standing matter waves', i.e. the same calculation as in the case of photons applies

$$g(j) dj = \pi j^2 dj$$

- we again consider the number of possible quantum numbers  $j_x, j_y, j_z$  in one quadrant of a spherical shell with radius  $j = (j_x^2 + j_y^2 + j_z^2)^{1/2}$  and thickness  $dj$
- here per set of spatial quantum numbers there are two different spin states  $m_s = \pm 1$  (spin up and spin down) similar to the two different polarizations for photons
- use relation between quantum number  $j$  and electron energy  $\epsilon$

phys4.16 Page 2

## Number of Free Electron States in a Metal

- relation between electron matter wave quantum number  $j^2 = (j_x, j_y, j_z)^2$  and electron energy  $\epsilon$  in a 3D box

$$j = \frac{2L}{\lambda} = \frac{2L}{h} p = \frac{2L}{h} \sqrt{2m\epsilon}$$

$$dj = \frac{L}{h} \sqrt{\frac{2m}{\epsilon}} d\epsilon$$

- using deBroglie wave length  $\lambda = \frac{h}{p}$  and  $p = \sqrt{2m\epsilon}$

- number of electron states at energy  $\epsilon$  in a volume  $V = L^3$

$$g(\epsilon) d\epsilon = \pi j^2 dj = \frac{8\sqrt{2} \pi L^3 m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

- this number of states is independent of the actual shape of the metal and only depends on its volume, i.e. the density of electrons in the metal

phys4.16 Page 3

## Fermi Energy

- calculate the total number of electrons at  $T = 0$  to find the Fermi energy  $\epsilon_F$

$$\begin{aligned} N &= \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{8\sqrt{2} \pi V m^{3/2}}{h^3} \int_0^{\epsilon_F} \sqrt{\epsilon} d\epsilon \\ &= \frac{16\sqrt{2} \pi V m^{3/2}}{3 h^3} \epsilon_F^{3/2} \end{aligned}$$

- thus the Fermi energy is given by

$$\epsilon_F = \frac{h^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3}$$

- depending only on the electron density  $n = N/V$

- Fermi energy in copper (Cu)

- free electron density

$$n = 8.48 \cdot 10^{28} \frac{1}{m^3} \quad \text{from density \& atomic mass}$$

- Fermi energy

$$\epsilon_F = 7.04 \text{ eV} = 85000 \text{ K}$$

- Fermi velocity

$$v_F = \sqrt{2\epsilon_F/m} \sim 1.6 \cdot 10^6 \frac{m}{s}$$

phys4.16 Page 4

## Electron Energy Distribution

- number of electrons at energy  $\epsilon$  at a thermal equilibrium temperature  $T$

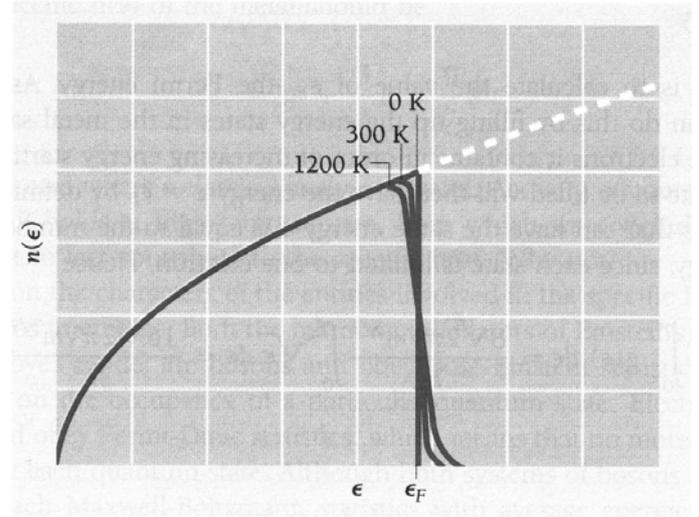
$$n(\epsilon) d\epsilon = g(\epsilon) f_{FD}(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V_m^{3/2}}{h^3} \frac{\sqrt{\epsilon}}{e^{(\epsilon-\epsilon_F)/kT} + 1} d\epsilon$$

with  $V_m^{3/2}$  expressed in terms of  $\epsilon_F$

$$= \frac{3N}{2} \frac{\epsilon_F^{-3/2}}{e^{(\epsilon-\epsilon_F)/kT} + 1} d\epsilon$$

- number of electrons (electron density) at different temperatures

- as the Fermi energy is usually very high compared to ambient temperature, the energy distribution of the electrons does vary only weakly with  $T$



phys4.16 Page 5

## Average Electron Energy

- total electron energy

$$E = \int_0^{\epsilon_F} \epsilon n(\epsilon) d\epsilon = \frac{3N}{2} \epsilon_F^{-3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon$$

$$= \frac{3}{5} N \epsilon_F$$

- average electron energy

$$\bar{\epsilon} = \frac{E}{N} = \frac{3}{5} \epsilon_F$$

- these average electron energies are very high, if the electrons were classical particles they would have to be at temperatures of several 10000 K to have these energies

- specific heat of electrons

$$C_{Ve} = \frac{\pi^2}{2} \frac{kT}{\epsilon_F} R$$

- the factor of  $kT/\epsilon_F$  makes this contribution small at room temperature

- at low temperatures  $C_{Ve} \sim T$  can dominate over  $C_V \sim T^3$

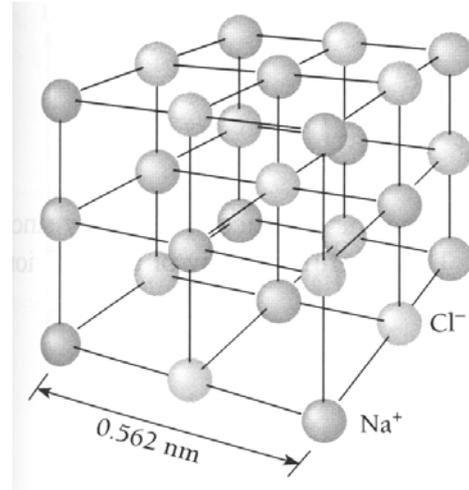
phys4.16 Page 6

## The Solid State

- most of the matter in the physical world around us (on earth) is in the solid state (which is not true for the universe as a whole)
- solids consist of atoms, ions or molecules closely packed together
- the binding occurs either by **covalent**, **ionic**, **van der Waals** or **metallic bonds** all of which are mediated by **electromagnetic forces**

structure:

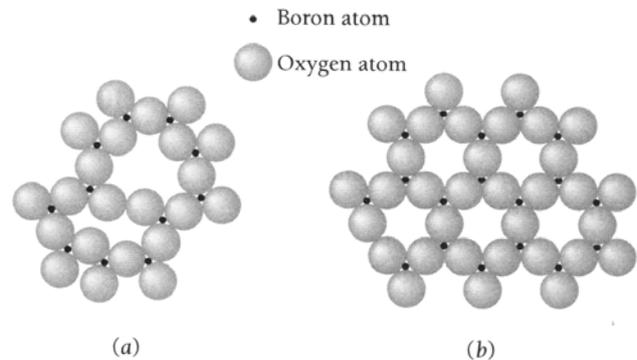
- many solids appear in **crystalline** structure, i.e. the constituents are arranged in a regular, repeated three dimensional pattern (a **lattice**) with **long range order**
- only few solids appear as single crystals (e.g. Silicon (Si)), most consist of very many small **crystallites**



phys4.16 Page 7

## Amorphous Solids

- some solids (e.g. glass, plastics) have an **amorphous** structure, i.e. they have no long range but only **short range order**
- can be viewed as a very viscous (glassy) liquid which crystallizes very slowly



- amorphous and crystalline  $B_2O_3$

melting:

- in amorphous solids the bond strengths varies throughout the material
- as a result melting occurs slowly and continuously
- in crystalline solids most of the bonds have equal strengths and thus melting occurs at a well defined temperature

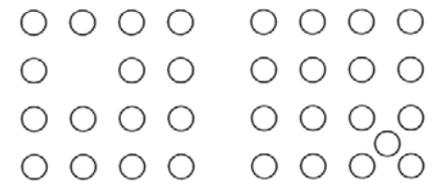
phys4.16 Page 8

## Crystal Defects

- most crystals have deviations from perfect regularity and symmetry which are called **defects**

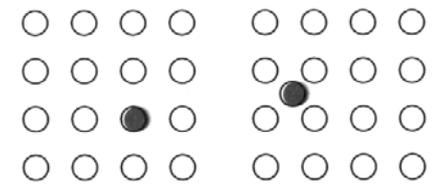
- one kind of imperfection is the **point defect** (see figure)

- they occur when (a) an atom is missing from the regular crystal structure (**vacancy**), (b) an additional atom of the same kind occurs (**interstitial**), (c) an impurity atom replaces an atom in the crystal (substitutional impurity) or (d) an impurity atom occurs at an interstitial position



(a)

(b)



(c)

(d)

- defects occur due to thermal excitation, due to irradiation, due to impurities present during the formation of the material

- large truly perfect crystals hardly exist (they can be pretty good though)

- single crystal Si (purity 1 ppb = part per billion =  $1/10^9$ ), see photograph

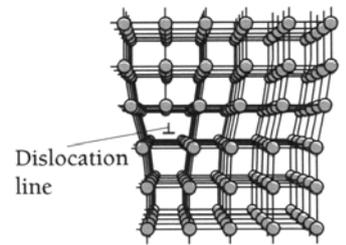
- diamond



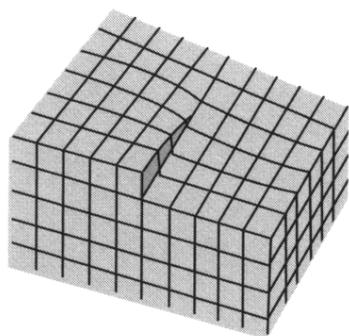
## Dislocations

- a **line defect** corresponds to a missing line of atoms in a crystal, see (a), it is called a **dislocation**

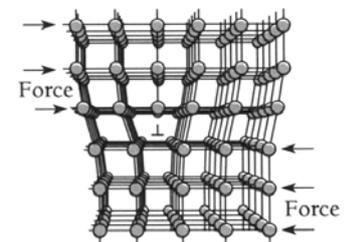
- the dislocation may move from inside the crystal towards an edge (see, b-c) releasing the stress from the crystal lattice



(a)



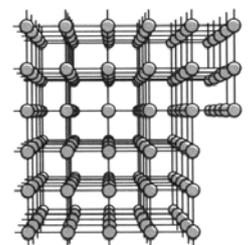
- **screw dislocation** (figure) arises when the crystal is continuously displaced along a cut into the crystal forming a screw like discontinuity in which the atomic layers spiral around a single point



(b)

- dislocations are created when solids are deformed

- some solids get harder when they contain many dislocation (**work hardening** in cold rolled sheet metal)

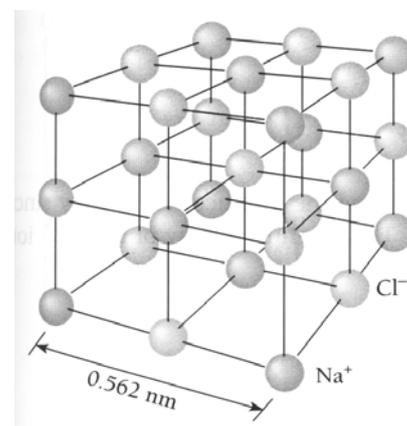


(c)

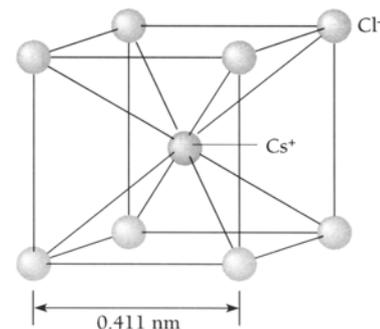
- **thermally annealed** crystals with less defects may be soft

## Ionic Crystals

- ionic crystals form between (a pair of) elements with low ionization energy and high electron affinity,
- electron affinity is the energy released by an atom when an electron is added to form a negatively charged ion
- in the ionic crystal sodium chloride (NaCl, see figure) one electron is transferred from Na (ionization energy 5.14 eV) to Cl (electron affinity 3.61 eV) forming ions  $\text{Na}^+$  and  $\text{Cl}^-$  which bind electrostatically when the total energy in the crystal is reduced from that of separate Na and Cl
- minimum ion-ion distance is determined by balance between Coulomb attraction and repulsion due to Pauli exclusion
- the **cohesive energy** is the energy per atom required to break a the crystal up into ions
- the cohesive energy is provided by the Coulomb attraction with the neighboring ions



face centered cubic NaCl



body centered cubic CsCl

phys4.16 Page 11

## Attractive Coulomb Potential

- find the total Coulomb energy  $u_0$  between one ion (e.g.  $\text{Na}^+$ ) and all its neighbors
- $u_0$  is determined by the number of ions (coordination number) present at a given distance  $r$  from the ion under consideration

- nearest neighbors  $u_1 = -6 \frac{e^2}{4\pi\epsilon_0 r}$  first coordination

- next nearest neighbors  $u_2 = +12 \frac{e^2}{4\pi\epsilon_0 \sqrt{2} r}$  second coordination

- summation over all nearest neighbors

$$u_c = \sum_{i=1}^{\infty} u_i = -\frac{e^2}{4\pi\epsilon_0 r} \left( 6 - \frac{12}{\sqrt{2}} + \dots \right) = -\alpha \frac{e^2}{4\pi\epsilon_0 r}$$

- with the Madelung constant  $\alpha \sim 1.748$  for NaCl and all other face centered cubic (fcc) ionic crystals
- for the body centered cubic (bcc) crystal CsCl the Madelung constant is  $\alpha \sim 1.763$
- all simple crystal structures have Madelung constants  $\alpha \sim 1.6 - 1.8$

phys4.16 Page 12

## Repulsive Potential

- repulsive force due to exclusion principle with effective potential

$$U_r = \frac{B}{r^n}$$

- short range force depending on a large power  $n \sim 8-10$  of the separation  $r$  between ions (empirical model)

- total energy

$$U = -\alpha \frac{e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

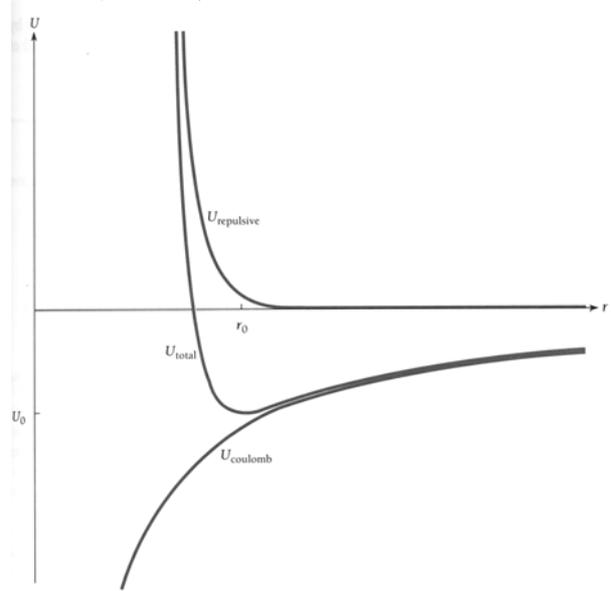
- equilibrium position

$$\left. \frac{\partial U}{\partial r} \right|_{r=r_0} = \alpha \frac{e^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} \stackrel{!}{=} 0$$

$$\Rightarrow B = \frac{\alpha e^2}{4\pi\epsilon_0 n} r_0^{n-1}$$

- total energy at equilibrium distance

$$U_0 = -\frac{\alpha e^2}{4\pi\epsilon_0} \frac{1}{r_0} \left(1 - \frac{1}{n}\right)$$



NaCl: to be reduced by  $E_i - E_{aff}$

$$r_0 = 0.281 \text{ nm} ; U_0 = -7.96 \text{ eV}$$

phys4.16 Page 13

## Properties of Ionic Crystals

- hard, due to ionic bonds

- high melting points due to large binding energy

- brittle, due to repulsive forces occurring with next nearest neighbor ions when dislocations are formed

- ionic crystals dissolve in polar solvents (water) but not in covalent solvents

- good electrical insulators, due to strong binding of electrons to ions

- transparent for visible radiation

- absorbing to infrared radiation exciting lattice vibrations in the ionic crystal

phys4.16 Page 14