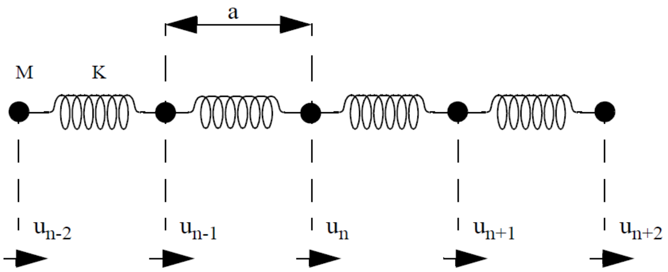
Multiple choice questions (10%):

There is only one correct answer for each of the questions below, marking more than one answer will count as a wrong answer.

a) Which crystal structure has the maximum packing fraction

1) bcc
2) hcp
3) fcc
4) both fcc and hcp

b) Consider the 1-dimensional linear chain in the figure below with N atoms in the chain. How many vibrational branches will be in the dispersion relation $\omega(k)$?



1) 6 branches
2) 3N-3 branches
3) 3N branches
4) 1 branch
5) 3 branches

c) Consider a one-dimensional solid with a lattice spacing of 0,32 nm. What is the value for the wavevector k at the zone boundary of the first Brillouin zone?

1) 8,17 nm^{-1}
2) 9,82 nm^{-1}
3) 10,43 nm^{-1}
4) 21,63 nm^{-1}

d) What is the main source of electron backscattering and thermalization in the Drude model?

1) electron-electron collisions
2) electron-electron and electron-ion collisions
3) electron-ion collisions
4) collisions with the wall of the crystal (finite dimensions)

e) Related to the previous question: What is the actual main source of backscattering in realistic solids?

1) electron-ion collisions
2) electron-phonon collisions
3) scattering on lattice imperfections/impurities
4) electron phonon and electron-ion collisions
5) electron-phonon collisions and scattering on lattice imperfections/impurities

f) Which of the experimental methods below is the best choice for determining phonon dispersion curves?

1) Inelastic neutron scattering
2) Transmission electron microscopy
3) x-ray diffraction
4) Scanning tunnel microscopy
5) Molecular beam epitaxy

g) Which electrons can contribute to the electrical and thermal conductivity in metals

1) all conduction electrons
2) only electrons that have an energy close to the Fermi energy E_F (approx. in an energy range of $4k_BT$ around E_F)
3) all electrons (both free electrons and electrons that are still bound to the ionic cores)
4) only electrons with an energy $\gg E_F$

h) Which statement is correct:
Phonons are:

1) Bosons
2) Fermions
3) Anions
4) they can be both Fermions or Bosons depending on the nuclear spin

i) What is meant by the expression ”the first Brillouin zone”?

1) The Wigner Seitz cell of the reciprocal lattice
2) The Bravais lattice of a reciprocal lattice
3) The diffraction area around the zeroth order peak in x-ray diffraction experiments
4) The area in reciprocal space that is enclosed by the Fermi energy E_F
5) The Wigner Seitz cell in hexagonal lattices

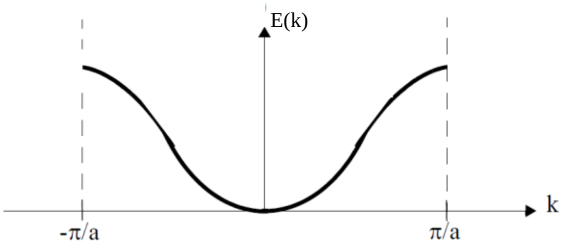
Introductory questions (15%):

Give brief answers to the following questions:

a) What is the difference between an intrinsic and an extrinsic semiconductor?

b) List the most common types of bonding in solids and give a brief description of each.

c) Describe the concept of the effective mass. The figure to the right shows an energy band. Make a sketch of the effective mass for this band.



d) Explain the terms *paramagnetism*, *diamagnetism* and *ferromagnetism*. In which kind of materials can the different types of magnetism be found and why?

e) What is a phonon? What is the difference between optical and acoustical phonons? How many acoustical and how many optical phonon branches can be found in a cubic crystal with two atoms in the basis?

Problem 1: structure and diffraction (20%)

a) The structure factor can be written as

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} f_j \cdot e^{(-i\boldsymbol{G}\cdot\boldsymbol{r}_j)}$$

Briefly explain the involved quantities.

b) Galliumarsenide crystalizes in one of the cubic lattice structures. In the unit cell the atoms take the following positions:

Ga: $000, \quad \frac{1}{2}\frac{1}{2}0, \quad \frac{1}{2}0\frac{1}{2}, \quad 0\frac{1}{2}\frac{1}{2}$

As: $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \quad \frac{3}{4}\frac{3}{4}\frac{1}{4}, \quad \frac{3}{4}\frac{1}{4}\frac{3}{4}, \quad \frac{1}{4}\frac{3}{4}\frac{3}{4}$

where all coordinates are given as with respect to the length of the unit cell a.

Which Bravais lattice is formed by the Ga atoms and which by the As atoms? What lattice is the complete crystal and what is the name of this crystal structure?

c) Calculate the structure factor for galliumarsenide for a general reflex **hkl**.

d) Which reflexes are systematically suppressed? The atomic form factors of Ga and As are very similar and therefore there will be additional reflexes that are very weak. Which reflexes are this?

Problem 2: phonons – thermal conductivity (10%):

In analogy to the kinetic theory of gases, one can find an expression for the thermal conductivity k of an insulator:

$$k = \frac{1}{3} C v l$$

Here C is the phonon heat capacity, v is the phonon velocity and l is the mean free path.

a) In insulators the thermal conductivity k decreases at high temperatures. What is the reason for this?

b) What is the temperature dependence of k at low temperatures in a perfect crystal?

Provide a brief explanation for each of your answers.

Problem 3: free electron model and energy bands (20%):

a) Give a brief overview on the free electron model: What properties does this model describe? For which material type is this model relevant? Draw a schematic plot of the electron dispersion $E(\boldsymbol{k})$ in the free electron model.

b) Blochs theorem states that the wavefunction of an electron in a periodic potential can be written as

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

with the real function $u_{\boldsymbol{k}}(\boldsymbol{r})$. What is the periodicity of this function?

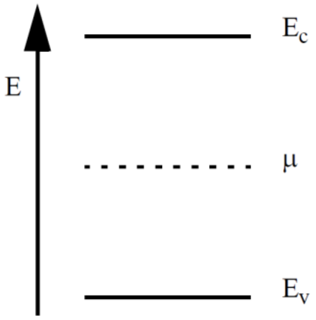
c) How is the electron dispersion in the free electron model modified when a periodic potential is taken into account? Consider both the case for a vanishingly small potential (also sometimes referred to as the empty lattice approximation) and a finite potential. Schematically draw the electron dispersion for both cases.

d) Describe a reason for the occurrence of energy bands and energy gaps (it is enough to describe one reason/approach here). Name an experimental technique to measure energy gaps in solids.

Problem 4: semiconductors (25%):

a) What distinguishes insulators, semiconductors and metals in terms of the band structure? Give a brief description and/or use a schematic to explain the differences.

b) The figure below is a schematic of the energy levels in an intrinsic semiconductor



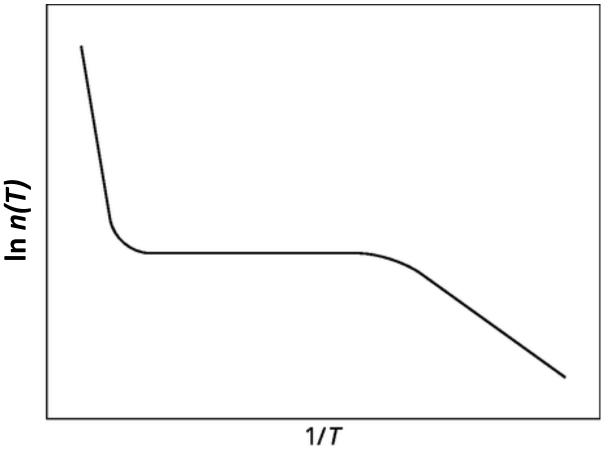
Find the concentration of holes at 300K in the above semiconductor if the band gap is 1,4 eV and the effective mass for holes is 40% of the free electron mass.

c) Find an expression for the hole concentration that is independent of the chemical potential μ.

d) How will the energy schematic from question b) change if we introduce n-dopants? Make a sketch of the modified energy schematic (assume that $T = 0$) and briefly explain the changes in comparison to the intrinsic case.

e) Find the position of the donor level in relation to the conduction band if the effective mass for electrons is $m^* = 0.1\ m_e$ and the dielectric constant is $\varepsilon = 10\ \varepsilon_0$.

f) The figure below shows the temperature dependence of the electron concentration of a n-doped semiconductor. Name and describe the different regions.



Appendix: Expressions and constants that might be useful for solving the exam:

$k_B = 1.38 \cdot 10^{-23} J/K$ $e = 1.6 \cdot 10^{-19} C$ $\varepsilon_0 = 8.85 \cdot 10^{-12} s^4 A^2 kg^{-1} m^{-3}$

$h = 6.63 \cdot 10^{-34}\, Js$ $m_e = 9.1 \cdot 10^{-31} kg$ $c = 3.0 \cdot 10^8\, m/s$

$\hbar = h/2\pi = 1.05 \cdot 10^{-34} Js$ $R_0 = 13.6\, eV$

$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1}$	Planck distribution law for phonons (average phonon occupation number)
$\omega(k) = 2\sqrt{\frac{K}{M}} \left\lvert \sin \frac{ka}{2} \right\rvert$	Phonon dispersion relation:
$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}$	3D free-electron density of states
$D(E) = \frac{mL^2}{\hbar^2 \pi}$	2D free-electron density of states
$E_n = -R_0/n^2$	energy levels of the hydrogen atom
$R_0 = \frac{e^4 m_e}{32\pi^2 \varepsilon_0^2 \hbar^2}$	the Rydberg constant
$f(E) = \frac{1}{e^{(E-\mu)/k_B + 1}}$	Fermi-Dirac distribution function (Fermi-function)

$$n = 2\left(\frac{2\pi m_e^* \cdot k_B T}{h^2} \right)^{\frac{3}{2}} e^{-(E_c - \mu)/k_B T} = N_c e^{-(E_c - \mu)/k_B T}$$

$$p = 2\left(\frac{2\pi m_h^* \cdot k_B T}{h^2} \right)^{\frac{3}{2}} e^{(E_v - \mu)/k_B T} = N_v e^{(E_v - \mu)/k_B T}$$

Suggested solution:

Multiple choice questions:

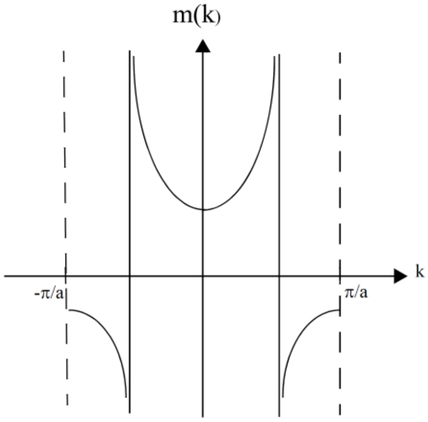
a) 4)
b) 4)
c) 2)
d) 3)
e) 5)
f) 1)
g) 2)
h) 1)
i) 1)

Introductory questions:

a) An intrinsic semiconductor is a pure semiconductor without any (or only very few) impurities. This results in an equal charge carrier concentration for electrons and holes and a position of the chemical potential in the middle of the band. An extrinsic semiconductor has charged impurity states (often deliberately introduced through doping). The charge carrier concentration is dependent on the amount of acceptor- or donator-atoms that were introduced. The position of the chemical potential is strongly dependent on the temperature and doping (see later problem)

b) - Van der Waals bonds: Interaction in materials with closed shells (noble gases) - attractive interaction due to dipole moments from the charge fluctuation in the shell (r^6), repulsive interaction when shells start to overlap because of Pauli exclusion principle (r^{12} or exponential)- complete potential is called the Lennard-Jones potential
- Ionic bond: bond formed by positive and negative ions through electrostatic force (both attractive and repulsive contributions). Can be described by the Madelung energy and constant. (This type of bond is most commonly found in I-VII crystals).
- Covalent bond: Attractive interaction formed by an overlap of the electron wave functions of different atoms. Needs quantum mechanical treatment and results in two states with different spin configuration (singlet or triplet). Generates antibonding and bonding states. Simplest example is the hydrogen molecule bond.
-metallic bond: ionic cores embedded in a sea of electrons. This lowers the electron energy and thus gives an attractive interaction. Metallic bonds are formed in materials with easily detachable outer electrons (e.g. group I, II and III materials).

c) The effective mass is a concept to integrate the properties of the periodic lattice into the free electron model. It is the modified mass of the electrons moving in bands. The effective mass is inversely proportional to the curvature of the band. This gives the following sketch for the effective mass in the band:



d) - Paramagentism: Materials with free magnetic moments from bound or free electrons will preferably align their magnetic moment with an external field. Only possible in materials with partly filled electron shells (3d or 4f materials)
- diamagnetism: is associated with induced magnetic moments in a magnetic field (the electrons partly "shield" the external field). The induced magnetic moment is always antiparallel to the applied external field. The correct description requires a quantum mechanical treatment, taking into account the vector potential, this leads to a B^2 term in the Hamiltonian of the Schrödinger equation, giving a paramagnetic contribution.
- ferromagnetism: Also needs free magnetic moments, so also unpaired shells e.g. in 3d or 4f materials. Here the local magnetic moments couple via an exchange interaction (similar to the hydrogen molecule). For ferromagnetic materials the exchange interaction favors parallel alignment of the magnetic moment. Ferromagnets can have a magnetization without an external magnetic field.

e) A phonon is the quantized energy particle of a lattice wave. Optical and acoustical branches refer to different branches in the dispersion relation. Acoustical phonons have a nearly linear dispersion around k=0 in the dispersion relation (sound waves), optical phonons have a finite ω at k=0, they can be excited optically. A cubic crystal with 2 atoms in the basis has 6 phonon dispersion branches, 3 optical and 3 acoustical.

Problem 1:

a) f_j is the atomic formfactor, it is an expression for the electron density of the atoms in the unit cell.
$\boldsymbol{G}$ is the reciprocal lattice vector (vector between reciprocal lattice points)
$\boldsymbol{r}_j$ is the coordinate of atom j
the summation index j goes over all atoms in a single unit cell

b) The Ga and the As atoms are positioned in a face centered cubic lattice (fcc). Also the complete GaAs crystal is fcc, now with two atoms in the basis. This type of crystal structure is called zincblende

c) $S = f_{Ga}\left[1 + e^{i\pi(\boldsymbol{h}+\boldsymbol{k})} + e^{i\pi(\boldsymbol{h}+\boldsymbol{l})} + e^{i\pi(\boldsymbol{k}+\boldsymbol{l})}\right] + f_{As} \cdot e^{\frac{i\pi}{2}(\boldsymbol{h}+\boldsymbol{k}+\boldsymbol{l})}\left[1 + e^{i\pi(\boldsymbol{h}+\boldsymbol{k})} + e^{i\pi(\boldsymbol{h}+\boldsymbol{l})} + e^{i\pi(\boldsymbol{k}+\boldsymbol{l})}\right]$

$$S = \left(f_{Ga} + f_{As} \cdot i^{\boldsymbol{h}+\boldsymbol{k}+\boldsymbol{l}}\right) \cdot \left[1 + (-1)^{\boldsymbol{h}+\boldsymbol{k}} + (-1)^{\boldsymbol{h}+\boldsymbol{l}} + (-1)^{\boldsymbol{k}+\boldsymbol{l}}\right]$$

d) The second factor becomes zero if the indices are mixed and 4 if the indices are all odd or all even. In that case
$S = 4\left(f_{Ga} + f_{As} \cdot i^{\boldsymbol{h}+\boldsymbol{k}+\boldsymbol{l}}\right)$
If $\boldsymbol{h} + \boldsymbol{k} + \boldsymbol{l} = 2 + 4m$ (remember only all odd or all even indices are allowed) this becomes
$S = 4(f_{Ga} - f_{As})$ and since $f_{Ga} \approx f_{As}$ these indices are very weak.

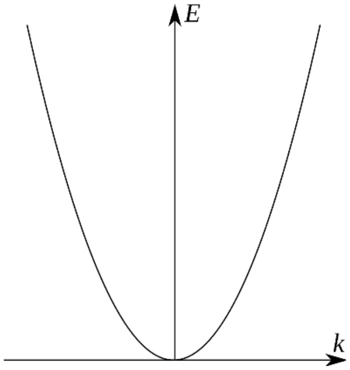
Problem 2:

a) The most important factor here is the mean free path l. The phonon heat capacity C is near constant at higher temperatures and the mean phonon velocity also varies little. The mean free path decreases at higher temperatures due to phonon-phonon scattering, $l \sim T^{-1}$. The main scattering source is Umklapp-scattering.

b) At low temperatures in small perfect crystals l is only limited by the system size (so no T dependence). The phonon velocity is nearly constant (speed of sound). The heat capacity $C \propto T^3$ at low temperatures (see also Debye approximation), so the thermal conductivity k is proportional to T^3.

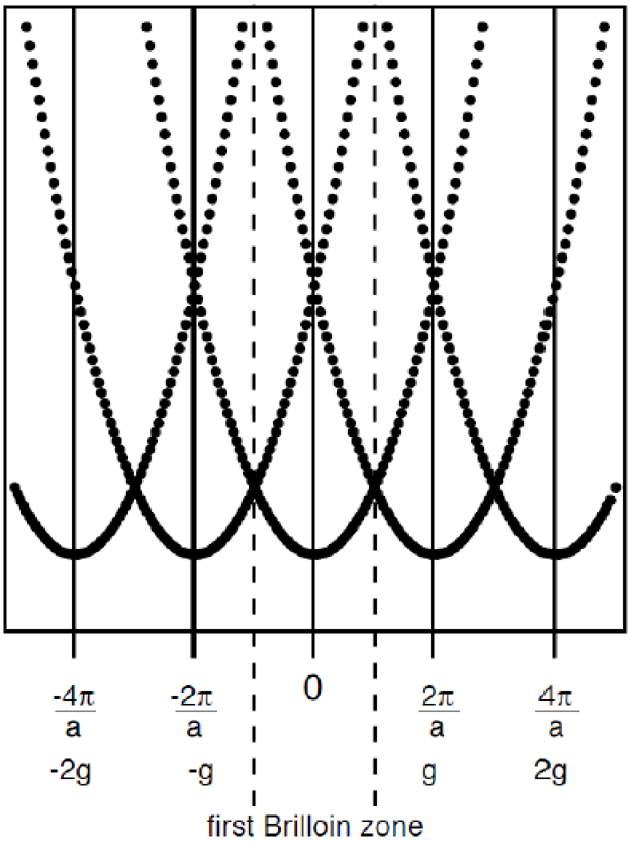
Problem 3:

a) The free electron model is based on the assumption of the conduction electrons behaving like a free electron gas. It mostly describes the kinetic properties (conductivity, heat conduction) well. The electrons do not interact with neither ion, lattice or with each other. The Pauli exclusion principle is taken into account. This model has been developed to describe the properties of metals. The electron dispersion is a parabolic function that follows the relation $E = \frac{\hbar^2 k^2}{2m}$:



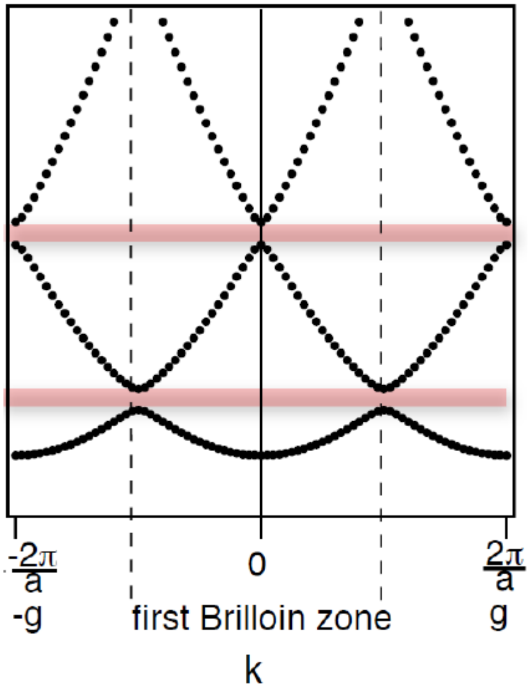
b) $u_{\boldsymbol{k}}(\boldsymbol{r})$ is lattice periodic.

c) The nearly free electron model gives us the following dispersion relation for a vanishingly small periodic potential:



➔ The periodic lattice potential results in a periodicity of the free electron dispersion.

If we now take a finite potential into account we will end up with this dispersion relation:

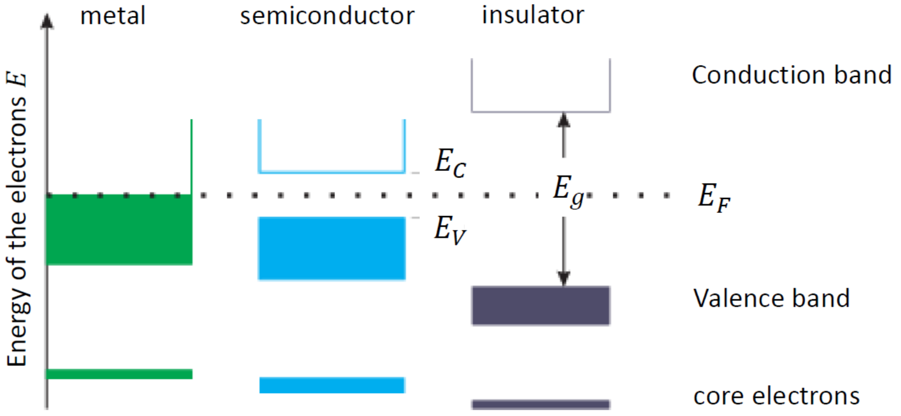


At the edge of the Brillouin zone we see band gaps develop and thus energy bands are forming. These bands have sine or cosine like dispersion.

d) Apart from the reasoning in the previous part of the solution, the occurrence of energy bands can also be reasoned from Bragg deflection off electrons that are traveling perpendicular to the crystals lattice planes. This reflection results in the formation of a standing wave which can be described by a forward and backwards moving wave which generate different electron densities in the lattice (one with a maximum on the position of the atoms and one between them). This results in a difference in energy for the two solutions, which is equivalent to an energy (band)gap. Another possibility is to look at the evolution from atomic orbitals to the energetic states in a crystal. In a crystal the energy levels of the individual atoms will overlap, especially the outermost energy levels. This overlap of orbitals leads to the formation of energy levels at slightly different energy for each of the involved atoms (similar to the formation of bonding and antibonding states in the hydrogen molecule). This will lead to the development of energy bands around the energetic position of the atomar energy levels.
Experimental techniques: Spectroscopy, ARPES, temperature activation of the conductivity

<u>Problem 4:</u>

a) - Metals are materials with partly filled bands, this means electrons can be easily excited into free states. They are therefore characterized by a high electrical conductivity.
- semiconductors have a completely filled band and the chemical potential is situated in a bandgap. The size of the bandgap to qualify as semiconductor is typically chosen as being up to 3eV (such that thermal excitation of carriers at room temperature is still noticeable). They conduct electricity badly.
- Insulators also have a completely filled band and the chemical potential is inside the bandgap. The size of the bandgap is however above 3eV, such that these materials are electrical insulators at room temperature.



b) The concentration n of holes in the valence band is of an intrinsic semiconductor at T=300K, an energy gap of 1,4eV (and $E_v - \mu \cong -0.7eV$) and an effective mass of 0.4*m$_e$ can be found by

$$p = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{\frac{3}{2}} e^{\frac{E_v-\mu}{k_B T}} = 1{,}1 \cdot 10^{13}\ \mathrm{m}^{-3}$$

As some of you noticed the energetic position of μ is of course temperature dependent (since $\mu = \frac{1}{2}E_g + \frac{3}{4}k_B T ln\left(\frac{m_p^*}{m_e^*}\right)$). The second term, which gives the temperature dependent correction, depends mostly on the ratio of the effective masses. For large effective mass ratios of e.g. 10 the correction is approx. 40 meV which would, however, result in a sizable correction to the carrier density due to it entering the exponential. Since I did not clearly state an effective mass for the electrons, I will accept the simple solution above as well as answers that state the temperature dependence. If I get the complete explanation, I stated here, you get bonus points.

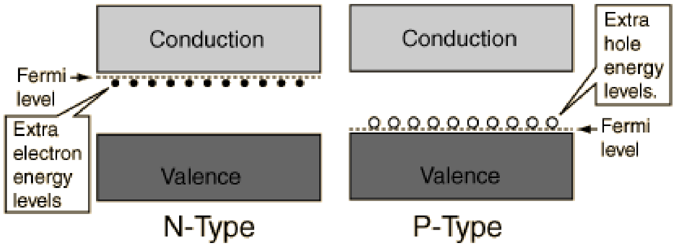
c) Here we can use the law of mass action:

$$np = 4\left(\frac{2\pi m_e^* \cdot k_B T}{h^2}\right)^3 (m_e^* m_p^*)^{3/2} \cdot e^{-E_g/k_B T})$$

and since in an intrinsic semiconductor $n_i = p_i$ we get

$$n_i = p_i = \sqrt{np} = 2\left(\frac{2\pi m_e^* \cdot k_B T}{h^2}\right)^{\frac{3}{2}} (m_e^* m_p^*)^{3/4} \cdot e^{-E_g/2k_B T})$$

d) n-dopants (or donors) are defect atoms with an extra electron compared to those of the semiconductor lattice. Introducing them into the crystal will result in easily excitable electrons, which can be represented in the band scheme by the introduction of an energy level with filled electron states close to the bottom of the conduction band. At T=0 the Fermi level is now located between the Donator level and the conduction band (and similarly with hole levels):



e) A good approximation for the energetic position of the donor level can be found from the hydrogen model. Here we can just take into account the modifications from the effective mass and the dielectric constant in the semiconductor to the Rydberg model:

$$E_d = \frac{m_e^*}{m_e \varepsilon^2} \cdot R_0 = 13{,}6 \text{ meV}$$

f) The temperature behavior can be divided into 3 different regions:

- freeze out – here the temperature is to low to fully ionize all the donors and E_F is between the donor energy level and the conduction band bottom.
- extrinsic - all donor levels are ionized but the temperature is low enough such that carrier excitation from the valence into the conduction band is negligible . E_F is moving towards the middle between conduction and valence band.
- intrinsic – here the temperature is high enough to excite carriers from the valence into the conduction band and the carrier concentration is dominated by this process. E_F is in the middle between conduction and valence band.