

# AD2

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## **ABSTRACT**

# 1 Introduction

Cadmium sulfide (CdS) is in the class II-VI semiconductor.

In 2.1 The free Electron Model we will use the free electron model to obtain some results for a given metal and describe some of the basic concepts. In the model it is assumed that the metal contains a large concentration of essentially free electrons. These assumptions lead to a satisfying description of many effects in metal, which are of great importance in our daily lives.

In 2.2 Energy Bands in Solids *Elementary Solid State Physics* [1] delivered insights in these concepts to get

In 2.3 Semiconductors

Semiconductor devices can display a range of useful properties, such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping, or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion.

## 2 Results

### 2.1 The free Electron Model

By using the free electron model, some of the parameter of a given metal can be calculated. The given metal crystallizes in the fcc structure with a lattice parameter for the conventional unit cell of  $0.409\text{nm}$ . And a given resistivity for room temperature.

(Source [1, Elementary Solid State Physics Chapter 4])

#### Collision Time

For calculating the collision time the following relation is used.

$$\sigma = \frac{Ne^2\tau}{m^*} \quad (1)$$

At it is a monovalent metal and the FCC-Unit cell contains 4 atoms the concentration of the conduction electrons  $N$  can be calculated as ( $a = 4.09\text{\AA}$ ):

$$N = \frac{4}{a^3}$$

So for the collision time  $\tau$  follows: With ( $m^* = m_0$ ) the free electron mass.

The electrical resistivity is given as:  $\rho = 2.13\mu\Omega\text{cm}$

which leads to a conductivity of  $\sigma = \frac{1}{\rho} = 4.695 \cdot 10^7 \frac{1}{\Omega\text{m}}$

$$\tau = \frac{\sigma \cdot m^* \cdot a^3}{4e^2} = 28.5 \cdot 10^{-14}\text{s}$$

#### Question 2

For a thin metal wire with a length of  $10\text{cm}$ , a square cross section with a side of  $0.1\text{mm}$  and a potential difference along the wire of  $0.2\text{V}$

The electric field  $E$  in the wire can be calculated as:

$$E = \frac{U}{L} = 2 \frac{V}{m}$$

As for the current density the following relations are known.

$$J = \sigma E \quad J = Nev_D$$

So for the drift velocity follows:

$$v_D = \frac{\sigma E}{Ne} = 1.003 \frac{m}{s}$$

### Question 3

In the free-electron model, the electron dispersion relation is,

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$$

Here  $m^*$  is the effective mass. At low temperature, all of the  $k$  states below the Fermi wave vector  $k_F$  are filled and all the states above  $k_F$  are empty. (see the next subsection)

The resistivity of a metal as a function can be best described;

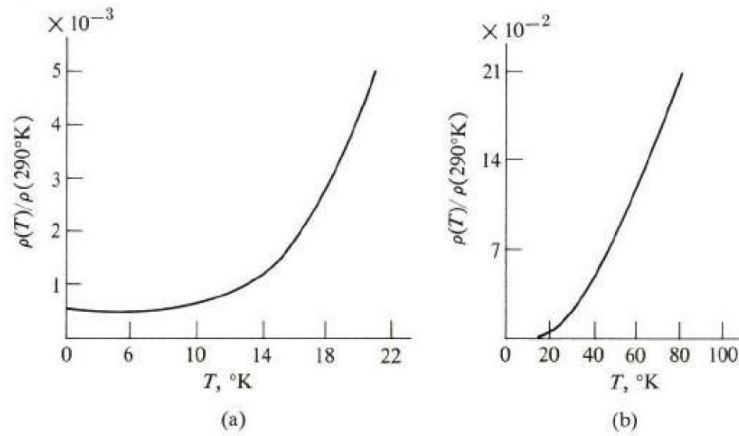


Figure 1: The normalized resistivity  $\rho(T)/\rho(290^\circ\text{K})$  versus  $T$  for Na in the low-temperature region (a), and at higher temperatures (b) [1, Elementary Solid State Physics p. 148]

At temperatures near  $0^\circ\text{K}$  the resistivity has a small constant value. The resistivity increases with  $T$  Figure 1 a. For higher values for  $T$  the value of the resistivity increases linear with  $T$ . Room temperature  $T = 300^\circ\text{K}$  usually falls in the linear region.

### Fermi

The energy of the electron in a metal is quantized according to quantum mechanics. As so they follow the *Pauli exclusion principle*, which means only two electrons with different spin can occupy one energy level. The highest occupied energy level is then called the Fermi energy or the fermi level.

The situation described obtains in metals as  $T = 0^\circ\text{K}$ . The probability that an level below the fermi energy is occupied is 1 and above equals 0.

If the system is heated, the electrons near the fermi level get excited as the electrons below the fermi level can not absorb energy due to the exclusion principle.

Which leads to the *Fermi-Dirac distribution*, which gives the probability that the level  $E$  is occupied by an electron

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (2)$$

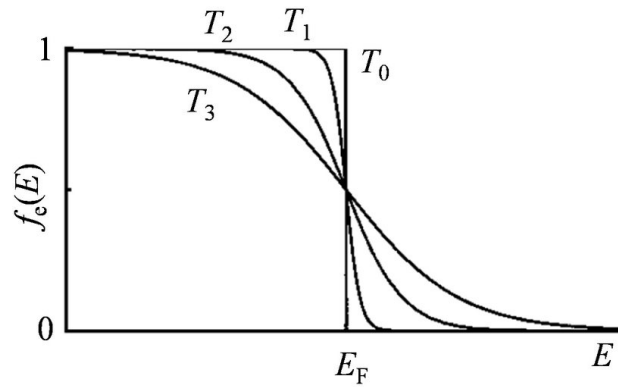


Figure 2: Fermi-Dirac distribution function at different temperatures:  $T_3 > T_2 > T_1$  (and  $T_0 = 0$  K). At the absolute zero temperature ( $T_0$ ), the probability of an electron to have an energy below the Fermi energy  $E_F$  is equal to 1, while the probability to have higher energy is zero. [3]

As the energy of an electron is entirely kinetic, it is possible to write the energy as:

$$E = \frac{1}{2} m^* v^2$$

As for the  $T = 0^\circ$  the fermi energy is the highest possible value a maximum velocity  $v_F$  of the particles can be found.

$$E_F = m^* v_F^2$$

This leads to a sphere in the three dimensional velocity space  $(v_x, v_y, v_z)$  the sphere has an radius of  $v_F$

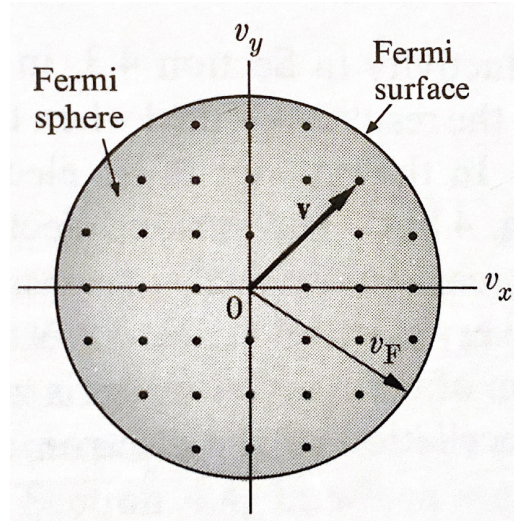


Figure 3: The Fermi surface and the Fermi sphere [1, Elementary Solid State Physics p. 268]

### Cyclotron Frequency

By applying a magnetic field to an metal, the electron inside are caused to move in a counter-clockwise circular fashion. The frequency is called the cyclotron frequency.

Figure 4 shows this schematically.

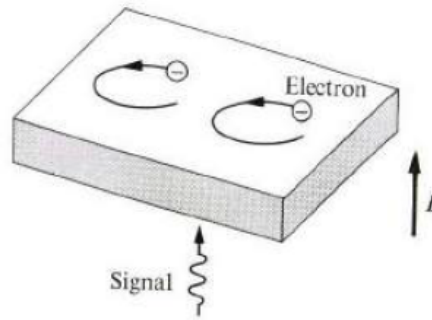


Figure 4: Cyclotron Motion [1, Elementary Solid State Physics p. 160]

The motion of an electron in a magnetic field can be described by the following differential equation.

$$-e(\vec{v} \times \vec{B}) = m \frac{d\vec{v}}{dt} \quad (3)$$

With the given information that  $\vec{B} = B\vec{z}$  The equation above lead to the following two equation.

$$-ev_y B = m \frac{d}{dt} v_x$$

$$ev_x B = m \frac{d}{dt} v_y$$

Which can be solved with the additional information

$$k(0) = k_{0x}$$

$$\vec{k} = k_{0x} \cos\left(\frac{eB}{m^*}t\right) \hat{x} + k_{0y} \sin\left(\frac{eB}{m^*}t\right) \hat{y}$$

This leads to the Cyclotron frequency of:

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

## Plasma Frequency

In the range of the plasma frequency the metallic medium acts like a nonabsorbing transparent dielectric. In Figure 5 the reflection coefficient of a metal in dependence of the angular frequency is shown. The plasma region is shown where the reflection coefficient is zero.

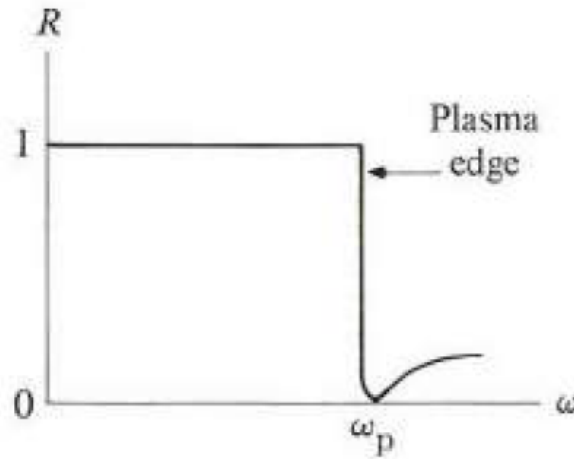


Figure 5: The plasma reflection edge. [1, Elementary Solid State Physics p. 166]

The plasma frequency can be calculated as:

$$\omega_P^2 = \frac{Ne^2}{\epsilon_L m^*} \Rightarrow \omega_P = \sqrt{\frac{Ne^2}{\epsilon_L m^*}} \quad (4)$$

With the parameter given  $m^* = m_0$  and  $\epsilon_L = \epsilon_0$ .

The plasma frequency can be calculated as:



$$w_P = 1.364 \cdot 10^{16} \frac{1}{s}$$

which corresponds to an energy of

$$E_P = \hbar\omega = 1.439 \cdot 10^{-23} J = 8.978 eV$$

## 2.2 Energy Bandy in Solids

### Bloch electron

Independent electrons which obey the one electron Schrödinger equation for a periodic potential are called Bloch electrons and obey Bloch's theorem. Own functions of  $\Psi_k(r)$  of the Hamiltonian in the field perfectly ideally periodic crystal lattice can be presented in the form of:

$$\Psi_k(r) = u_k(r) \exp(ik \cdot r) \quad (5)$$

, where  $u_k(r)$  is a function with periodicity of the network, i.e.

$$u_k(r) = u_k(r + R_n) \quad (6)$$

for all Bravais  $R_n$  vectors. Note that from the above formulas it follows that

$$\Psi_k(r + R_n) = u_k(r) \exp[ik \cdot (r + R_n)] = \Psi_k(r) \exp ik \cdot R_n$$

This relationship allows an alternative formulation of Bloch's theorem: own functions Hamiltonian, a perfectly periodic crystal lattice can be represented in such a way that each of them corresponded to a certain wave vector  $k$ , with

$$\Psi_k(r + R_n) = \Psi_k(r) \exp(ik \cdot R_n)$$

Bloch's theorem makes it easier to determine the electron's wave functions in a crystal, because that's enough be limited to one unit cell, while the original wave function in the equation Schrödinger applies to the whole crystal.

### Free electron model

The free electron model allows to describe, for example, specific heat, thermal conductivity and thermal expansion. This model, however, does not include where observed differences come from between metals, semiconductors and insulators. To this end, necessary is to take into account the periodic structure of the crystal, which leads to periodically changing potential in which the electrons move in the crystal. The most important feature of the extended the model is the prediction of electron energy bands, separated by gaps. The crystal is an insulator when the allowed energy bands are completely empty or completely planted. If one of the permitted bands is partially filled, then the crystal behaves like a metal. Where one or two bands are planted only in slightly or very little crystal is a semiconductor

### Question 3

$$\vec{v} = \frac{1}{\hbar} \nabla_k E(\vec{k})$$

$$v_x = \frac{1}{\hbar} \frac{d}{dk_x} E - E_0 [\cos(k_x a) + 1] = \frac{E_0 a}{\hbar} \sin(k_x a)$$

As for the mass follows from:

$$E = \frac{\hbar^2 k^2}{2m^*} \rightarrow m^* = \frac{\hbar k_x}{v_x} = \frac{k_x}{\sin(k_x a)} \cdot \frac{h}{E_0 a}$$

For  $E_0 = 1$  and  $a = 1$  the graphs are shown in the following.

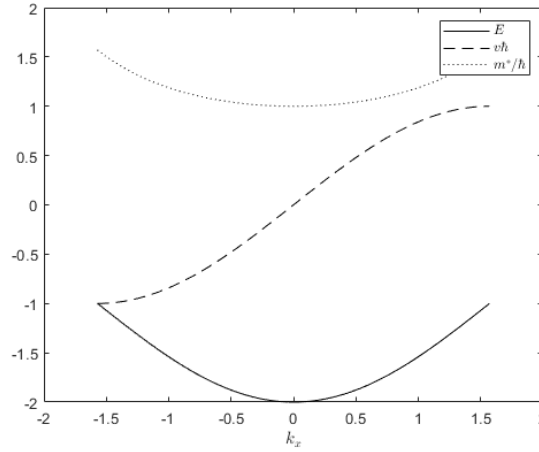


Figure 6: Energy, Velocity in x direction and reduced mass as a funktion of k

### Kronig–Penney model

The Kronig-Penney model [1] is a simplified model for an electron in a one-dimensional periodic potential. The possible states that the electron can occupy are determined by the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V(x) \Psi = E \Psi \quad (7)$$

In the case of the Kronig-Penney model, the potential  $V(x)$  is a periodic square wave.

## 2.3 Semiconductors

(Source [1, Elementary Solid State Physics Chapter 6])

### Question 1

The carrier distribution function in CB für an intrinsic semiconductor is given as the product:

$$g_e(E)f(E)$$

with

$$g_e(E) = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar} \right)^{\frac{3}{2}} (E - E_C)^{\frac{1}{2}}$$

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \approx e^{-\frac{E-E_F}{k_B T}}$$

So for the maximum

$$\frac{d}{dE} \left( \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar} \right)^{\frac{3}{2}} (E - E_C)^{\frac{1}{2}} e^{-\frac{E-E_F}{k_B T}} \right) = 0$$

By dividing through the constant factors:

$$\frac{d}{dE} \left( (E - E_C)^{\frac{1}{2}} e^{-\frac{E-E_F}{k_B T}} \right) = 0$$

$$\frac{1}{2} (E - E_C)^{-\frac{1}{2}} e^{-\frac{E-E_F}{k_B T}} + \frac{-1}{k_B T} (E - E_C)^{\frac{1}{2}} e^{-\frac{E-E_F}{k_B T}} = 0$$

And finally

$$E = E_C + \frac{k_B T}{2}$$

### Question 2

For the effective density of states in the conduction band the following relation is known:

$$N_c = 2 \left( \frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$$

Which lead to the following result

$$N_c = 2.415 \cdot 10^{24} \frac{1}{m^3}$$

In the same manner also the density of states in the valence band can be calculated.

$$N_v = 2 \left( \frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$$
$$N_v = 1.796 \cdot 10^{25} \frac{1}{m^3}$$

In an intrinsic semiconductor the concentration of the holes and the electron are equal and this concentration is named as intrinsic carrier's concentration.

Which is known to be:

$$n_i = p_i = 2 \left( \frac{k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} e^{-\frac{E_g}{2k_B T}}$$
$$n_i = p_i = 0.959 \cdot 10^3 \frac{1}{m^3}$$

For the intrinsic Fermi can be calculated as

$$E_{Fi} = \frac{E_g}{2} + \frac{3}{4} k_B T \ln \left( \frac{m_h^*}{m_e^*} \right)$$
$$E_{Fi} = 1.326 eV$$

The temperature dependence for both the effective density of states in the CB and VB is proportional to  $T^{3/2}$  so both will increase with the temperature.

The intrinsic carrier concentration  $n_i$  is proportional to

$$n_i T^{3/2} \exp\left(-\frac{1}{T}\right)$$

which means for  $T \gg 0^\circ K$  the same temperature dependence as for the effective density of states.

The intrinsic fermi level increases linearly with  $T$

### Question 3

If the given semiconductor CdS was doped p-type with a concentration of  $10^{15}$  acceptor impurities the following about the concentration and holes at  $T = 0^\circ K$  can be said.

At this point the thermal energy becomes too small to cause electron excitation, which means that all electrons fall from the conduction Band into the donor level. Also the conductivity

goes to zero. This process is called freeze out. So for the concentration of electron and holes at  $T = 0^\circ K$

The concentration of the electrons:

$$n(T = 0^\circ K) = 0$$

As the semiconductor is doped with holes the concentration of the holes is the same as it was initially.

$$p(T = 0^\circ K) = 10^{15} \text{ cm}^{-3}$$

#### Question 4

As the concentration of acceptor impurities is much higher than the holes concentration of the intrinsic semiconductor ( $10^{15} \frac{1}{\text{cm}^3} \gg p_i$ )

The concentration of the holes in the semiconductor is equal to concentration of the impurities.

$$p = 10^{15} \frac{1}{\text{cm}^3} = 10^{18} \frac{1}{\text{m}^3}$$

As the square of the intrinsic concentration  $n_i$  is equal to the product of the sum of the concentration of the holes and the concentration of the electrons.

$$np = n_i^2$$

$$n = \frac{n_i^2}{p} = \frac{(0.959 \cdot 10^3 \frac{1}{\text{m}^3})^2}{10^{18} \frac{1}{\text{m}^3}} = 9.197 \cdot 10^{-13} \frac{1}{\text{m}^3}$$

As for calculating  $(E_F - E_{Fi})$  the temperature dependence of the concentration on electrons and holes can be used:

$$n = n_i e^{\frac{E_F - E_{Fi}}{k_B T}} \quad p = n_i e^{-\frac{E_F - E_{Fi}}{k_B T}}$$

Which leads to:

$$(E_F - E_{Fi}) = \ln\left(\frac{n}{n_i}\right) \cdot k_B T$$

$$(E_F - E_{Fi}) = -0.896 \text{ eV}$$

Also the following could be said about  $E_F$  by increasing the concentration of the dopant the Fermi Level in a p-type semiconductor will move to the valence band.

By increasing the temperature the Fermi Level will move towards the middle of the gap.

### Question 5

As the potential for Hole is given as:

$$V(r) = -\frac{e^2}{4\pi\epsilon_r\epsilon_0 r} \quad (8)$$

By using the Bohr model, the binding energy can be found, which corresponds to the ground state of the acceptor and calculated. With using  $\epsilon_r = 8.9$  and  $m_h = 0.80 m_0$

$$E_a = \frac{1}{\epsilon_r^2} \left( \frac{m_h}{m_0} \right) \underbrace{\left[ \frac{e^4 m_0}{2(4\pi\epsilon_h \hbar)^2} \right]}_{13.6eV}$$

$$E_a = 0.14eV$$

Figure 7 shows the acceptor level inside the energy gap.

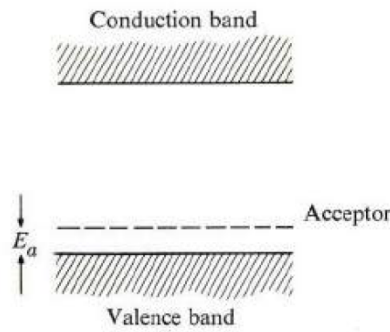


Figure 7: The acceptor level in a semiconductor [1, Elementary Solid State Physics p. 268]

### Compensated semiconductor Question 6

Compensated semiconductor are those in which donors and acceptors are related in such a way that their opposing electrical effects are partially cancelled. In the compensated semiconductor there are additional sources of current carriers and therefore

$$n - p = \Delta n \neq 0.$$

Fermi energy value  $\epsilon_F$  in the doped semiconductor will change relative to  $\epsilon_{F(i)}$  values for an intrinsic semiconductor. From here we can write the equation

$$n = n_i \exp \left[ + \frac{\epsilon_F - \epsilon_{F(i)}}{k_B T} \right] \text{ and } p = p_i \exp \left[ - \frac{\epsilon_F - \epsilon_{F(i)}}{k_B T} \right]$$

Taking both of those formulas we get this relation

$$\frac{\Delta n}{n_i} = 2 \sinh \left[ \frac{\epsilon_F - \epsilon_{F(i)}}{k_B T} \right] \quad (9)$$

In donor semiconductors  $\Delta n > 0$  so Fermi energy  $\epsilon_F > \epsilon_{F(i)}$

In acceptor semiconductors  $\Delta n < 0$  so Fermi energy  $\epsilon_F < \epsilon_{F(i)}$

### Intrinsic resistivity Question 7

In order to determine resistivity of the intrinsic cadmium sulfide (CdS) at 300 K, proceed as follows. In an intrinsic semiconductor electron carrier concentration  $n$  equals to hole concentration  $p$  and this both equals intrinsic carrier concentration  $n_i$ . That is

$$n = p = n_i$$

The resistivity  $\rho$  of the intrinsic semiconductor is given by

$$\rho_{intrinsic} = \frac{1}{q(\mu_n n + \mu_p p)}$$

where charge  $q = 1.6 \times 10^{-19}$  C, electron mobility is  $\mu_n$  and hole mobility is  $\mu_p$ .

$$CalculationS \quad (10)$$

### Direct and Indirect Band Gab Question 8

In Figure 8 the Band Gab structure  $E(\vec{k})$  for CdS and ZnS as a model result is showed.

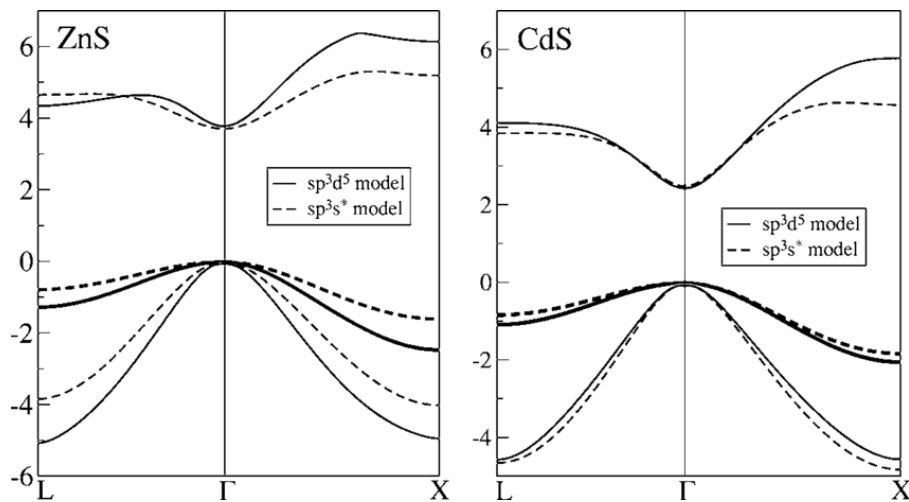


Figure 8: Bulk band structure for ZnS and CdS along the-L 111 and the-X 100 directions obtained with the sp 3 d 5 model solid line and the sp 3 s \* model of Lippens [6]



As the minimum of the conduction band as well as the maximum of the valence band are both at  $\Gamma$  ( $\vec{k} = 0$ ). CdS can be identified as a semiconductor with direct Band Gap.

As the Band Gap Energy is minimal at  $k = 0$ , it will increase with  $T$  due to the added kinetic energy to the electrons.

The Band Gap Energy can be easily measured by use of the fact that below the  $E_G$  no or only little absorption occurs.

By measuring the absorption coefficient  $\alpha$  in a semiconductor as a function of  $h\nu$  an edge will appear where  $\alpha$  rapidly raises. At this energy the electron can move to the conduction band and absorb the photon.

### Free excitation Question 9

An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

### P-N junction Question 10

A  $P - N$  junction is the juxtaposition of a n-type and a p-type piece of semiconductor, taken originally from the same block of crystal. The difference between the densities of donors and acceptors  $ND - NA$  undergoes a very sharp variation from a negative value in the  $P$  region to a positive value in the  $N$  region. An abrupt junction is by definition a junction in which the doping type changes over a very small distance compared to the spatial extent of the depletion region. When the junction meets thermal equilibrium, the Fermi energy has a constant value throughout the whole device. The energies of conduction and valence bands are therefore shifted up or down, and exhibit a smooth variation across the depletion region. As a consequence, there is an electrostatic potential energy difference appearing between the  $P$  and  $N$  region, equal to  $qV_d$ .

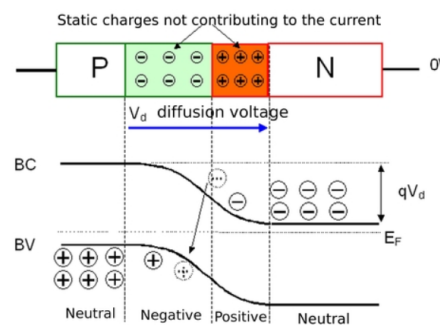


Figure 9: Energy diagram of a PN junction at thermal equilibrium [4]

For a p-n junction, letting  $C_A(x)$  and  $C_D(x)$  be the concentrations of acceptor and donor atoms

respectively, and letting  $N_0(x)$  and  $P_0(x)$  be the equilibrium concentrations of electrons and holes respectively, yields, by Poisson's equation:

$$-\frac{d^2V}{dx^2} = \frac{\rho}{\epsilon} = \frac{q}{\epsilon}[(P_0 - N_0) + (C_D - C_A)]$$

where  $V$  is the electric potential,  $\rho$  is the charge density,  $\epsilon$  is permittivity and  $q$  is the magnitude of the electron charge. Letting  $d_p$  be the width of the depletion region within the p-side, and letting  $d_n$  be the width of the depletion region within the n-side, it must be that

$$d_p C_A = d_n C_D$$

because the total charge on either side of the depletion region must cancel out. Therefore, letting  $D$  and  $\Delta V$  represent the entire depletion region and the potential difference across it,

$$\Delta V = \int \int \frac{q}{\epsilon}[(P_0 - N_0) + (C_D - C_A)] dx dx = \frac{C_A C_D}{C_A + C_D} \frac{q}{2\epsilon} (d_p + d_n)^2$$

where  $P_0 = N_0 = 0$  because we are in the depletion region. And thus, letting  $d$  be the total width of the depletion region, we get

$$d = \sqrt{\frac{2\epsilon}{q} \frac{C_A + C_D}{C_A C_D} \Delta V}$$

$\Delta V$  can be written as  $\Delta V_0 + \Delta V_{ext}$ , where we have broken up the voltage difference into the equilibrium plus external components. The equilibrium potential results from diffusion forces, and thus we can calculate  $V$  by implementing the Einstein relation and assuming the semiconductor is nondegenerate

$$V = \frac{k_B T}{e} \ln \left( \frac{n_n}{n_p} \right)$$

### 3 Conclusion

This report

For a given monovalent metal which crystals in the FFC structure with a unit cell size of  $a = 4.09\text{\AA}$  the collision time could be calculated as:

$$\tau = 28.5 \cdot 10^{-14} s$$

Also an expression for the cyclotron frequency could be obtained

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

The value of the intrinsic fermi level for CdS was found to be

$$E_{Fi} = 1.326 eV$$

as well as the intrinsic carrier concentration is

$$n_i = 0.959 \cdot 10^3 \frac{1}{m^3}$$

Figure 8 was used to identify Cadmium Sulfide as a direct Band Gap semiconductor.

## References

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- [3] METAL OXIDE PHOTOCATALYTIC NANOSTRUCTURES FABRICATED BY DYNAMIC SHADOWING GROWTH - Scientific Figure on ResearchGate. Available from: [https://www.researchgate.net/figure/Fermi-Dirac-distribution-function-at-different-temperatures-T3-T2T1-and-T0-0-K-At\\_fig2\\_280311898](https://www.researchgate.net/figure/Fermi-Dirac-distribution-function-at-different-temperatures-T3-T2T1-and-T0-0-K-At_fig2_280311898) [ accessed 16 Jun, 2020 ]
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