

F4

Optical properties of quantum wells and color centers

The aim of the exercise are optical measurements of quantum wells and the chromium ion inside the cubic lattice, including: absorption, luminescence and luminescence excitation spectra at room temperature and in liquid nitrogen. Based on the measurements, individual intra-center transitions should be identified and their shift as a function of temperature determined.

1. What you should know before experiment?

1. General knowledge of solid state physics: [1, 2].
 - a) Crystal structure and band model, band structure $E(k)$.
 - b) Lattice oscillations, phonons, phonon dispersion.
2. Optical properties: [1, 2, 3, 4]
 - a) Absorption mechanisms and their ranges.
 - b) Recombination mechanisms, luminescence.
 - c) Selection rules for optical transitions.
3. Quantum wells. Electron in rectangular and triangular (electric field) potential. The energy level. Optical transitions. [6]
4. Deep defects. Crystal field theory [1, 7]
5. Basic information about optical measurements [8]:
 - a) Principles of operation and construction of a monochromator,
 - b) Basis of CCD detector and camera.

It is advised to read the text, understand and widen your knowledge on words written in bold.

1. Absorption and emission of light

Light is an electromagnetic wave, propagating according to **Maxwell's equations**. In the material medium, the speed of the wave decreases. If the medium absorbs energy, the intensity of the wave propagating along the axis z , $I(z)$, decays in accordance with the formula (Bouguer-Lambert law):

$$I(z) = I(0)\exp(-\alpha z), \quad (1.3)$$

where α is **absorption coefficient**, $I(0)$ –intensity at interface. The α dependence on the wavelength, frequency or energy of photons is called the absorption spectrum.

Absorption of the photon can cause energy dissipation as a heat or an electron transition to the excited state, for example: ${}^4A_2 \rightarrow {}^4T_2$. The excited electron can fall into the basic state emitting light in a spontaneous (luminescence) or forced (in lasers) transition. We also have other methods of excitation, which lead to occupation that is not in accordance with thermodynamic equilibrium (non-thermal). Luminescence is spontaneous emission during the transition from a non-thermally excited quantum state. It is important to separate the absorption and emission processes. If the emission occurs during the action of an exciting factor (scattering, generation of higher harmonics or synchrotron radiation), then we do not talk about luminescence.

Separation of the absorption and emission processes (sometimes only by 10^{-14} s) allows us to distinguish the excited state and the final state. By studying the photons emitted in this way, we can learn about the quantum states between which transitions occur. Conventionally, a division is introduced

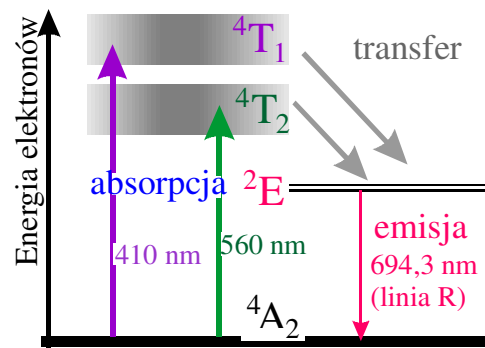


Fig. 1. The Jabłoński diagram presenting electron transitions in ruby.

into fast fluorescence (when the lifetime $\tau < 1 \mu\text{s}$) and slow phosphorescence ($\tau > 1 \mu\text{s}$). Depending on the method of excitation, luminescence can be divided into photoluminescence (excitation by light), electroluminescence (excitation by charge flow), chemoluminescence, bioluminescence, etc.

An example of absorption and luminescence transitions is shown in Figure 1. The diagram illustrating transitions between quantum states is called the Jablonski diagram. It can be seen that in addition to optical transitions, we must take into account energy transfer, which generally takes place non-radiatively. A simple observation of the diagram leads to the conclusion that in the case of emission, the energy of photons will generally be lower than in the case of absorption (Stokes' rule). Both the probability of absorption and the intensity of luminescence depend on **the oscillator strength** for a given transition. The oscillator strength, on the other hand, is proportional to the square of the transition moment between states. We can estimate it by knowing the **quantum selection rules** (discussed in the lecture "Quantum Mechanics and Chemistry" in the second year).

2. The investigated objects

In crystalline solids, electrons are in a periodic potential. As a result, their wave functions have the form of a **Bloch function**. This form allows for the possibility of **electron** motion, although the molecules it describes have unexpected properties - their masses differ from the mass of an electron in a vacuum, and their charges can be positive. The dependence of their energy, E , on momentum, $p = \hbar k$, $E(k)$, is called a **band structure**.

We distinguish between a **valence band**, containing positively charged molecules, i.e. **holes**, and a **conduction band**, in which negatively charged electrons (correctly **quasi-electrons**) are located. These bands are separated by an energy gap. The width of the energy gap in a semiconductor ranges from 0 eV (CdHgTe) to over 5 eV (AlN, diamond). Semiconductors differ from metals in that at zero temperature, they have a completely filled valence band and a completely empty conduction band.

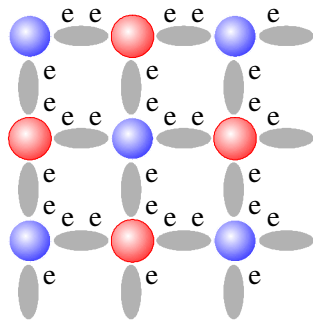


Fig. 2. Schematic diagram of bond occupancy by electrons in III-V material. Each atom has 4 bonds, each can be occupied by 2 electrons. Group III atoms provide 3 electrons, and group V atoms provide 5. Thanks to this, the number of electrons is equal to the number of states in the valence band.

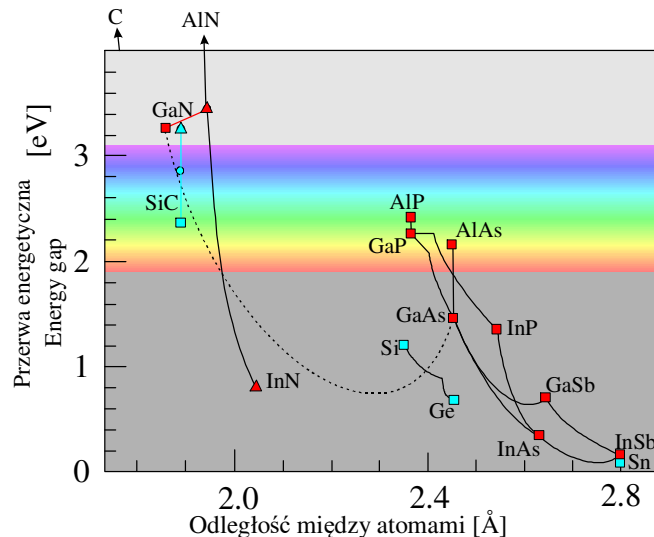


Fig. 3. Map of group IV (C, Si, Ge, Sn) and III-V (other) semiconductors. It can be seen that the heavier the constituent elements are, the narrower the energy gap is.

With the help of epitaxy, semiconductor structures can be produced from materials with different energy gap widths, for example, they are selected from different materials from the III-V group. Figure 2 shows the structure, and in Fig. 3 you can see the "map" of these materials. Materials with different cations can be mixed, e.g. InN with GaN gives a semiconductor alloy (GaIn)N. The parameters of such ternary alloys are marked in Fig. 3 by lines connecting the given binary compounds. If a thin (thickness L

of the order of 10 nm) layer of a material with a narrow energy gap is surrounded by a material with a wider gap, then only a two-dimensional (2D) space called a quantum well will be available for electrons. Such wells are used, for example, in light-emitting diodes (LEDs).

We will study quantum well luminescence using the example of samples with quantum wells made of (GaIn)N [9] and barriers made of GaN. GaN is a piezoelectric material and diodes based on this material have a built-in strong electric field. This field, acting on electrons, causes their energy to decrease (Stark effect). After applying voltage, we reduce this field, which increases the emission energy [10]. GaN is a very hard material and the difficulties in its production are comparable to obtaining diamond, but the devices produced are very durable. Blue diodes are particularly important, because when equipped with a phosphor, they can emit white light. The efficiency of such lighting is much higher than that of light bulbs, so the introduction of white light-emitting diodes has resulted in huge savings on a global scale. In 2014, the Nobel Prize was awarded for the development of the technique for obtaining GaN-based light-emitting diodes.

Energy of carriers in a rectangular quantum well is increased by quantization energy E_n :

$$E_n = \frac{n^2 \hbar^2}{8L^2 m^*}, \quad (2)$$

where $n = 1, 2, \dots$ - successive levels in the well.

An electric field, F , is created in the p-n junction (in a diode) and in piezoelectric materials (e.g. in GaN). The electron potential in this field increases linearly: $U(x) = eFx$. Thus, the electric field will turn a rectangular quantum well into a triangular one, as in Fig. 4.

An interesting situation will arise when two quantum wells are placed next to each other, separated by d . The electric field will cause the potentials of these wells to differ by:

$$\Delta U = eFd. \quad (3)$$

If indirect recombination occurs in such wells (an electron from the first well recombines with a hole from the second), the emission energy will be reduced by ΔU .

By stimulating the crystal with light, we create electric charges that partially screen the field, which will reduce ΔU and increase the energy of the emitted light. During this exercise, we will measure GaN/(GaIn)N/GaN wells grown at the Institute of High Pressure "Unipress".

Ruby ($\text{Al}_2\text{O}_3:\text{Cr}$) is a variety of the mineral corundum, Al_2O_3 , doped with chromium. Pure corundum is transparent to visible light and UV to 9 eV energy. Ruby, thanks to the admixture of Cr, has a red color and other optical properties that made it widely used in the production of lasers.

YAG - yttrium-aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$, does not occur in nature. YAG:Cr crystals that are in our laboratory were grown in ITME (Institute of Electronic Materials Technology) in Warsaw. YAG crystals are used in optics and laser production. Pure YAG crystal is colorless and with chromium is green.

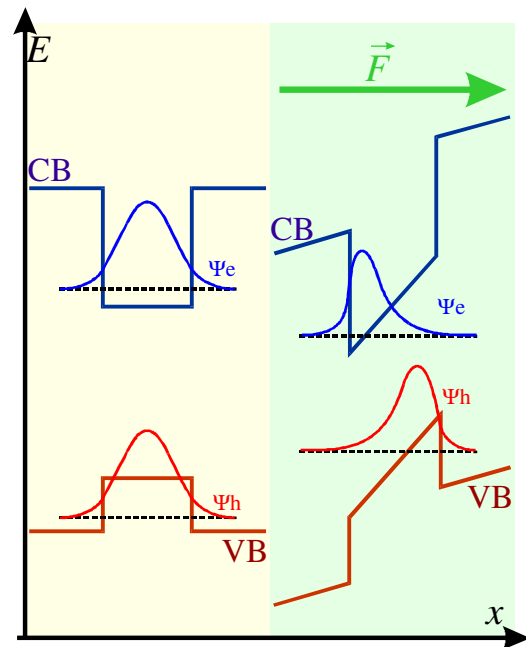


Fig. 4. Quantum well without field (left) and in electric field right. The field changes potentials to triangular and moves electrons and holes, reducing their energy difference.

The cloud of valence electrons surrounding the atom is described by a wave function that can correspond to several well-defined energies.

In the case of Cr^{3+} ion, the valence shell has the $3d^3$ configuration. State 4F is the ground state, 4P i 2G are excited states (we use here **spectroscopic notation**, the nX record means the state with multiplicity n and symmetry X).

Dopant ions have small radii (for example Cr^{3+} radius is 1.3 \AA) and when they are inside crystal, field generated by surrounding ions (ligands) can be treated as perturbation. This perturbation leads to level splitting by **crystal field**. Since chromium surroundings in ruby has octahedral **symmetry** (O_h), Cr wave functions have symmetries A_1 , A_2 , E , T_1 or T_2 .

The impact of the crystal field can be parameterized via the Dq/B ratio (Dq - crystal field splitting, B - electron interaction energy). Energy graph of individual levels as function of the crystal field is called **Tanabe –Sugano diagram** (see Fig. 1). The intensity of the crystal field depends on the crystal in which the Cr^{3+} ion is immersed. In our case, the simplest relation can be observed between the splitting parameter Dq , and energy of the ${}^4T_2 \rightarrow {}^4A_2$ transition:

$$E({}^4T_2) = 10 Dq. \quad (1.1)$$

The diagram allows comparing of the similar states in different crystals and also for the given crystal in different temperatures. While crystal is cooled, inter-atomic distances shrink, influence of the crystal field is stronger and the states shift in the diagram to the left. Additionally, we need to take into account influence of lattice oscillations (**phonons**). Ion - phonon interaction leads to the **line broadening** and generation of phonon replicas of electronic transitions.

The examples of electron transitions are plotted in Fig. 1 (page 1). Absorption of the photon causes the electron transition to the excited state, for example: ${}^4A_2 \rightarrow {}^4T_2$. The excited electron can fall into the basic state emitting light in a spontaneous (luminescence) or forced (in lasers) transition. For example, line R_1 that is used in lasers this is the ruby transition: ${}^2E \rightarrow {}^4A_2$. Electron can relax to lower level (example: ${}^4T_2 \rightarrow {}^2E$) transferring energy to lattice oscillations (**phonons**) and then it emits photon from the. In general, the energy of the emitted photon is smaller than the energy of the absorbed photon.

Electron transitions can be coupled with ion and crystal oscillations. We then observe oscillatory lines **or phonon replicas**. If the electronic transition is accompanied by phonon emission (or transition to a higher oscillatory level), the photon emitted will have less energy and in addition to the main emission line, we will observe a peak sequence or emission band with lower energy.

At high temperatures, the electron transition is sometimes accompanied by absorption of the phonon (or transition to a lower oscillatory level). Then the photon emitted has higher energy. The phonon replicas of lower energy are called Stokes lines and the lines of higher energy are called antistokes lines.

In the case of emission spectra, we generally observe bands with energy lower than the energy of the baseline (zero-phonon). In the case of absorption spectra, we generally observe bands with energy higher than the energy of the baseline (zero-phonon).

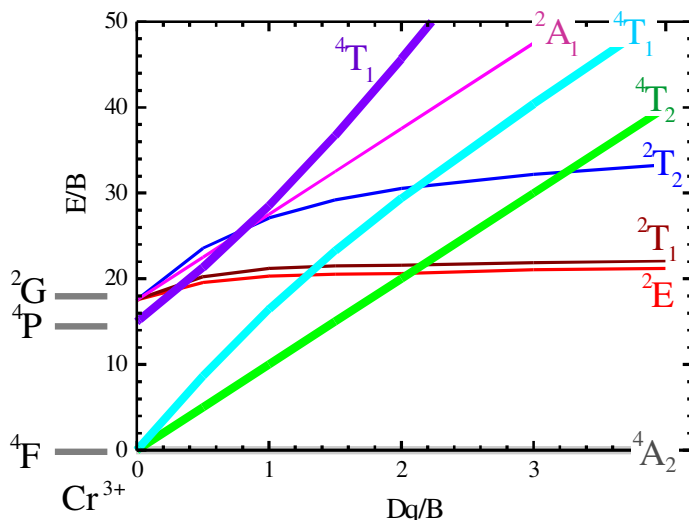


Fig. 1. Simplified Tanabe-Sugano diagram showing Cr^{3+} level splitting.[11], [12]

<http://wwwchem.uwimona.edu.jm:1104/courses/Tanabe-Sugano/TanSugd3.html>

3. The course of the exercise

- A. Preparing the computer spectrometer system: setting the exposure time and loading the background spectrum. The exposure time should be selected in such a way as to fully utilize the CCD camera registers. These activities are repeated before each subsequent measurement.
- B. Measurements of the spectra of 2 LED diodes with quantum wells as a function of voltage and current. The power supply allows for regulating the voltage and current, the values of which are read from multimeters. We set the power supply so that the diode current is in the range of 0.05 to 2 mA. We record the electroluminescence (EL) spectra with the spectrometer, paying attention to the intensity and position of the EL peak.
- C. Measurements of the photoluminescence (PL) spectra of two layers with quantum wells as a function of power. We stimulate the photoluminescence with a laser and record it using a spectrometer. It is necessary to ensure good focusing of the laser beam. We change the intensity of the stimulating light using gray filters. We start by measuring the PL spectrum without a filter, then we insert successive, increasingly stronger filters until the signal is lost. The filters are described by giving the optical density OD. The filter transmission is:

$$T = 10^{-OD}. \quad (5)$$

For example, OD = 0.3, means transition of 50%, and OD = 1, gives T = 10%.

- D. Measurement of the photoluminescence spectra of crystals with chromium (ruby and garnet). Photoluminescence is stimulated with a laser and recorded using a spectrometer.
- E. Measurement of the optical absorption spectra of ruby and garnet. The crystals are illuminated with a lamp. We record the spectrum of the lamp and the spectrum of light that passed through the crystal. In this measurement, special attention should be paid to subtracting the background and minimizing noise, because the most interesting part of the spectrum is in the range with the smallest amount of transmitted light. This range corresponds to the strongest absorption.
- F. We repeat the measurements of luminescence and absorption of crystals with chromium on samples placed in a cryostat in liquid nitrogen.
- G. Measurement of the photoluminescence excitation spectra (PLE) for the R line of ruby and garnet. The samples are stimulated with light from a monochromator. We perform measurements in the range of 400 - 640 nm, every 10 - 15 nm.

3. Report preparation

Report should be composed of the following parts:

1. Abstract,
 2. Theoretical introduction,
 3. Description of the measurement system and samples,
 4. Results and their analysis,
 5. Summary containing conclusions.
- Ad. 1. The summary should be short (a few sentences), but it should contain a description of the experiences and the most important results and conclusions.
 - Ad. 2. It is important to introduce diagram of quantum states and explain notation (e.g. symmetries and multiplicity), allowed and forbidden transitions, etc. The most important equations and their explanation used should be provided.
 - Ad. 3. In the description of the system, drawings should be present. Setups for measurements of electroluminescence, photoluminescence, absorption and excitation spectra are different and so should have separate schemes and descriptions.
 - Ad. 4. As the results of the measurements, we get electroluminescence, photoluminescence, transmission (absorption) spectra, and luminescence excitation spectra (PLE). For quantum wells we determine the dependence of light intensity on current intensity (by fitting a straight line) and

the energy of emitted light on voltage. Photon energies $h\nu$, in eV are calculated based on the wavelength λ measured in nm, using the formula:

$$h\nu = 1240 \text{ nm eV} / \lambda, \quad (6)$$

In the case of a quantum well, we prepare a graph of intensity and energy from the excitation power. Assuming the width of the well is $d = 1.06 \text{ nm}$ and 5.2 nm , based on equation (3), we should discuss the dependence of the electric field in the well on the voltage (for a diode) or excitation power for a layer without electrical contacts.

The absorption should be plotted in the form of $\alpha(\lambda)$ graphs. Assuming that for $\lambda = 750 \text{ nm}$ the absorption is zero, we correct results for reflection and geometry factor.

Identify the absorption and luminescence transitions and describe the lines. Compare spectra of luminescence and absorption in measured in room and liquid nitrogen temperatures. and determine the temperature shifts of the peaks. For the luminescence R line (${}^2E \rightarrow {}^4A_2$ transition), the exact position determination of the peak requires the Lorentz curve fitting:

$$I(E) = \frac{\beta\Gamma/2}{(E - E_0)^2 + (\Gamma/2)^2}, \quad (7)$$

where: E_0 – position, Γ – width a β – height of the peak.

The positions and widths of absorption and luminescence peaks should be determined. The changes induced by temperature should be discussed based on the formula for the $E_g(T)$ relationship (in the case of a diode) and the Tanabe-Sugano diagram (crystals). How do lines involving phonons change their intensity?

Determine the energy of the zero-phonon transition line ${}^4A_2 \rightarrow {}^4T_2$ in liquid nitrogen and calculate crystal field splitting Dq for Cr^{3+} in ruby and yttrium garnet (YAG) using equation (1.1).

The photoluminescence excitation spectrum should be compared with the absorption spectrum then similarities and differences should be discussed.

Ad. 5. Physical (scientific) significance of own results should be presented.

When preparing the description, remember to number equations (1) and figures (see Fig. 1). When using materials (texts, drawings, and programs) from other authors, a reference [1] should be placed in the text, and finally a list of cited sources (author, title, website address, etc.).

4. Literature

Handbooks:

- [1] J. Ginter - „Wstęp do fizyki atomu, cząsteczki i ciała stałego.” rozdz. I, III i IV
- [2] K. W. Szalimowa - „Fizyka półprzewodników”
- [3] C. Kittel - „Introduction to solid State Physics.”
- [4] T. S. Moss - „Optical properties of semiconductors”
- [5] J. I. Pankove - „Zjawiska optyczne w półprzewodnikach.”
- [6] L. I. Schiff – Quantum mechanics, chapter 2.
- [7] F. A. Cotton - „, Teoria grup. Zastosowanie w chemii.”
- [8] Wikipedia: monochromator, camera CCD.

Journals:

- [9] Shuji Nakamura, "InGaN-based blue light-emitting diodes and laser diodes", J. Crystal Growth **201–202**, 290 (1999) (<https://www.sciencedirect.com/science/article/pii/S002202489801344X>)
- [10] G. Muziol, *et al.* " Beyond Quantum Efficiency Limitations Originating from the Piezoelectric Polarization in Light-Emitting Devices", ACS Photonics **6**, 1963 (2019) DOI: 10.1021/acsp Photonics.9b00327
- [11] Zanatta *et al.* "Thermally synthesized ruby microstructures and luminescence centers", J. Appl. Phys. **100**, 113112 (2006)

Web:

- [12] <http://wwwchem.uwimona.edu.jm:1104/courses/Tanabe-Sugano/TanSug3.html>

K.K., 23 I 2025

Appendix CCD

Principle of operation of a CCD camera

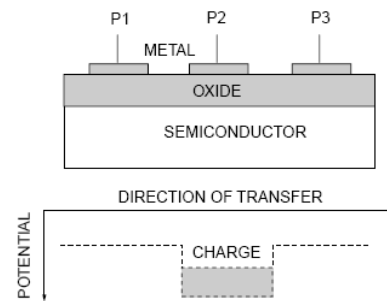
A CCD camera is a matrix of semiconductor detectors (usually photodiodes), the signal of which is recorded using CCD (Charge Coupled Device) registers.

Light is converted into an electrical signal in photodiodes. A strong electric field prevails in the area of the photodiode junction. Electron-hole pairs generated by photons absorbed in this area are separated by the field. The holes migrate to the substrate, electrons accumulate in the cathode. The charge generated in this way is then moved through charge-coupled circuits and counted by registers.

The principle of operation of charge-coupled circuits is based on closing or opening channels in a semiconductor layer covered with an insulator. The channels are opened or closed by applying a potential to the electrodes placed on the dielectric.

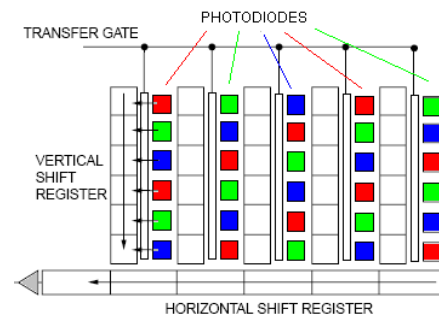
Principle of using charge-coupled device (CCD) circuits to record optical signals in a CCD camera:

1. Cross-section of a transmission line with CCD coupling. A negative potential is applied to electrodes P1 and P3, which blocks the flow of charge accumulated under electrode P2. A change in the potential, for example, at electrode P3 will cause the charge to flow to the right.



2. The structure of a CCD camera seen from above.

The photodiodes are arranged in columns. The electrode grid controls the transfer of charge first in columns and then in rows.



Registers of the CCD camera count the charge using a digital method. If the lighting is too weak or the exposure time is too short, we will get zeros or a small number of bits in the registers, which will make the signal step-like. In popular cameras, registers are usually 8-bit (count from 0 to 255). In measuring devices, we encounter registers from 10 to 16 bits (16 bits correspond to 0 - 65535). When choosing the exposure time, we should make sure, how many bit registers we have and remember not to exceed the maximum value of the register.

The measurement program reads each register many times and averages the results. If we average a single register m times, we get an average number of counts $n_s \pm \delta n_s$, where:

$$n_s = \Sigma n_i / m, \quad (C1)$$

$$\delta n_s = \frac{\sqrt{\Sigma n_i}}{m} = \sqrt{\frac{n_s}{m}}. \quad (C2)$$

As can be seen, with the increase in the number of averaging, the uncertainty of the average decreases.

