F7
Time-resolved photoluminescence spectroscopy

The objective of the present experiment in the measurement of the absorption response and the dynamics of luminescence of dopants in a crystal environment. The experiments are designed to allow the identification of electronic transitions and to define their lifetimes. From a physicist, time-resolved spectroscopy is a powerful tool to obtain information about the band (and crystal) structure of semiconductors. However, time-resolved techniques have many other uses, e.g. as probes of chemical and biological processes.

1. **What should you know before attempting the experiment?**
   - **I.** Basic knowledge of solid state physics [1, 2]:
     a. Crystal structure and its relation to the electronic band structure E(**k**),
     b. Crystal structure and its relation to lattice oscillations and phonon dispersion relation,
   - **II.** Optical properties [1, 2, 3, 4, 5]:
     a. Absorption mechanisms for photons, and when they occur,
     b. Recombination, luminescence and stimulated emission,
     c. Selection rules for optical transitions,
   - **III.** Deep impurity states. Crystal field theory [1, 6, 7, 9]
   - **IV.** Basic techniques for optical measurements [10, 11]:
     a. Inner workings of a monochromator,
     b. Principle of operation of oscilloscopes.

To prepare for the experiment, you should be familiar with the text below. Special attention should be paid to terms and words in **bold** letters.

YAG – Yttrium aluminum garnet $Y_2Al_5O_{12}$ does not occur naturally. Here, crystals of Cr:YAG (Cr-doped YAG) will be used, which were grown by colleagues from ITME (Institute of Technology for Electronic Materials, in a free translation). Such materials are routinely used as active media for solid-state **lasers**. Undoped YAG crystals show no coloration in the visible range (i.e. they are "glass-like"). However, Cr-doped crystals exhibit a green coloration. **Ruby** (Al_2O_3:Cr) is a variation of the mineral known as Corundum, Al_2O_3, where Cr is added as an impurity. Similarly, to YAG, undoped corundum is colorless and transparent in the visible range, for photons with energies up to 9 eV (how much is this in nm?). When doped with Cr, however, this material also becomes suitable for laser production. Lastly, zinc sulfide (ZnS) – a mineral known as sphalerite – is a II-VI semiconductor with a 3.6 eV energy gap. Impurities (dopants) in this material make it a good emitter in the green wavelength range. ZnS:Cu is (was), therefore, routinely used as a fluorescent medium for **CRT screens** (see how earlier oscilloscopes and cathode-tube-based televisions were built).

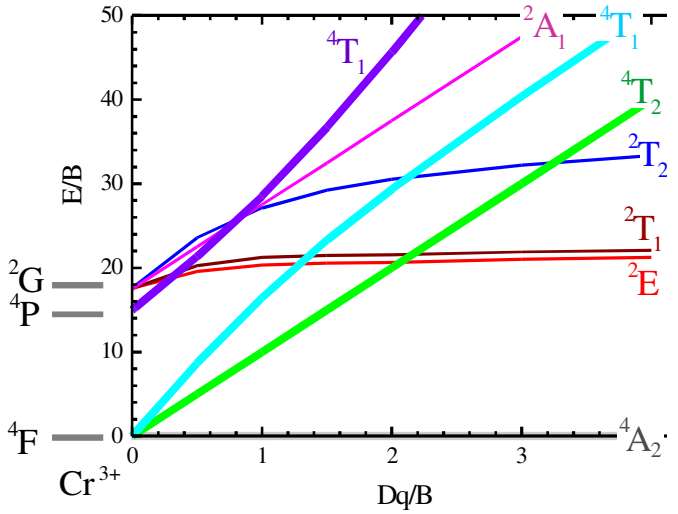

Figure 1 – Tanabe-Sugano diagram showing the energy level splitting of Cr^{3+} ions in a crystalline field
http://wwwchem.uwimona.edu.jm:1104/courses/Tanabe-Sugano/TanSugd3.html

Electrons belonging to a material's **valence band** can be described as wavefunctions composed by few (several) hybridized states with similar energies, belonging to the highest energy (half-filled) electronic orbitals of the atoms composing the solid. For Cu^{2+} ions, electrons in the outermost occupied orbital have electronic configuration $3d^9$, whereas Cr^{3+} electrons have a $3d^3$ configuration.

The electronic configuration $3d^9$ is composed by states with ^2D symmetry (using the **spectroscopic notation**, where ^nX represents a state with symmetry X and multiplicity n – see "group theory"). Electronic ground states in the $3d^3$ configuration are of ^4F symmetry, whereas excited states can be written as a superposition of ^4P and ^2G states. Impurity (dopant) ions considered here

have small atomic radii (e.g. Cr^{3+} has a 1.3 A atomic radius), and they can be treated as a small impurity in the crystalline field generated by all other elements composing the crystal (i.e., its presence does not change fundamental crystal parameters).

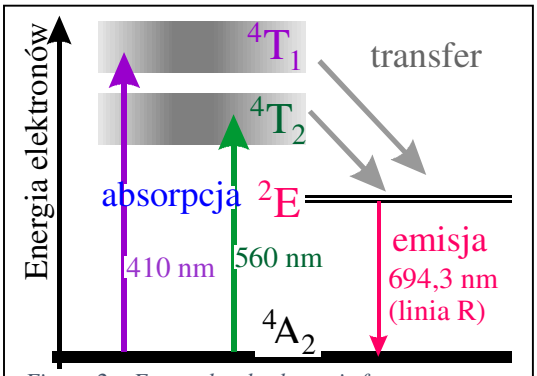

Figure 2 – Energy level schematic for energy bands and electronic transitions in a ruby laser

Distortions of the local (chemical) ionic environment lead to the splitting of the energy levels of ions. Such a phenomenon can be caused by different factors, among which is the presence of a **crystalline field**. For Cu^{2+} ions in a **tetrahedral chemical environment** (T_d), states initially in the ^2D state are split into ground states with symmetry $^2T_{2g}$ and excited states of symmetry ^2E_g. The chemical environment of Cr in ruby has **octahedral symmetry** (O_h), and the wavefunctions of electrons in the outermost electron shell assume symmetries of the type A_1, A_2, E, T_1, and T_2. The contribution due to the crystalline field may be parametrized through the quantity Dq/B, where Dq is the splitting generated by the crystalline field and B is the difference in energy associated to it. The energy-crystalline field diagram representing such a splitting is termed a **Tanabe-Sugano (TS) diagram**. Such a set of curves allows the comparison of emission lines originating from the same energy level of an impurity on different crystals, or of the same crystal at different temperatures (see Fig. 1). For example, if a crystal undergoes a phase transition where interatomic distances are reduced, leading to enhanced local crystalline fields, the energy levels associated to the impurity are displaced to the right in the TS diagram.

In the case of intense crystalline fields with spherical symmetry, the strongest electric fields to which impurities (dopants) are subjected might arise from another ionized impurities (dopants). If the electron-hole recombination occurs between the charge carriers of donors and acceptors, respectively, it will be very sensitive to such electric fields (e.g. as in ZnS:Cu). However, the electric field distribution will be at random, as dopants are usually randomly distributed over a lattice. Therefore, the effect will be stronger or weaker, depending on the spatial distribution of **donor-acceptor pairs** in the solid. This leads to wider emission lines/bands. Donor-acceptor pairs with smaller binding Energy are either further apart, or are subjected to stronger electric fields (also called "screening fields"). For them, emission lifetimes are longer. Donor-acceptor pairs with stronger binding energy, on the other hand, will undergo emission earlier. Therefore, the emission line's energy (and its width) will strongly depend on the time elapsed after the absorption event, with a monotonic decrease of emitted photon energies over time.

Light is an electromagnetic wave, thus obeying the **Maxwell equations**. When interacting with matter, it might be subjected to three processes: absorption, spontaneous emission, or induced emission. Spontaneous emission is caused by the recombination of carriers in excited states, whose population variation dn over a time interval dt can be written as $dn = r \times n \times dt$ (r is termed the recombination rate). If a recombination efficiency η is taken into account, the intensity of such an emission (also called luminescence) is given by $I = \eta dn/dt$. In this case, the time dependency of the luminescence can be described as

$$I(t) = I(0)\exp(-rt) = I(0)\exp\left(-\frac{t}{\tau}\right), \qquad (1.1)$$

where $\tau \equiv 1/r$ is defined as the **luminescence lifetime.**

Atoms in the ground state tend to absorb incoming light. Atoms in the excited state tend to emit light. For stimulated emission to be triggered, a situation known as **"population inversion"** is necessary. This is achieved whenever more atoms encounter themselves in an excited state. The attainment of such a scenario is impeded by spontaneous emission, which is a fast recombination process (in the ns timescale) that forces atoms towards their ground state. At the same time, according to **selection rules**, some excited energy levels are metastable – i.e., electrons on them have relatively large lifetimes (few μs or even ms), causing a difficulty to excite carriers from the ground state to the excited state (which remain occupied). It is possible to bypass both such obstacles by considering a system with three energy levels: (a) a ground state, (b) a short-lived excited state subjected to strong absorption from the ground-state and which decays non-radiatively to (c) a metastable long-lived state. The latter is populated from carriers both excited from (a) and decaying from (b). The population of excited states in (b) is larger than (a), and therefore such state is subjected to stimulated radiative recombination towards the ground state.

Such a set of energy levels (see Fig. 2) occurs, amongst other materials, in ruby. According to selection rules, the lifetime τ of the state ^{4}T is short (because ^{4}T→ ^{4}A transitions are permitted), of the order of 50 ns. However, the state ^{2}E has a long lifetime, leading to a population inversion in relation to the ground state. Ruby lasers were one of the first solid-state lasers ever constructed, being obtained in the 1960's by Theodore Maim.

The transition probability per unit of time for an initial state |j> to undergo a transition to a |i> state, when the system is subjected to a time-dependent perturbation is given by the Fermi golden rule

$$\frac{1}{\tau} = \frac{\mathrm{DOS}}{\mathrm{h}} H_{ij} H_{ji}, \qquad (1.2)$$

where $H_{ij} \equiv e < i|x|j >$ is the matrix element associated with the transition, τ is the **lifetime** of state |j> prior to the transition to |i> and DOS is the density of states associated with the transition, in units of energy^{-1}. Whenever a transition takes place between states of high symmetry, the matrix element H_{ij} can be virtually zero. In this case, the **transition is dubbed as forbidden**, and the lifetimes can be rather large.

Usually, the following transitions are considered as forbidden:

- Transitions between two states with even or odd symmetry. This occurs because the operator x is odd (i.e., if |a> is even, |b>=x|a> will be odd, and <a|b> = 0).

- Transitions between states with different spin multiplicity (the operator x does not operates over spin).

In the latter case, there should be no transitions between the states ^{2}E→^{4}A$_2$. Such a transition, however, can be mediated through interactions with other electrons in the crystal.

Electronic transitions might also be mediated through ionic or atomic oscillations in the crystal. In these cases, **oscillatory lines** are observed, as well as **phonon sidebands**. Whenever the electronic transition leads to the creation of a **phonon** (or the transition of the lattice to an oscillatory state with a higher **energy level**), the emitted photon will have a smaller energy than the absorbed one. In this case, a series of lines (or bands) will be observed with lower energies in comparison to the main emission line. At high temperatures, electronic transitions have a higher chance to occur after the emitting electrons absorb a phonon (or the lattice transitions to a state of lower energy). In this case, emitted photons will have higher energy than the main emission line.

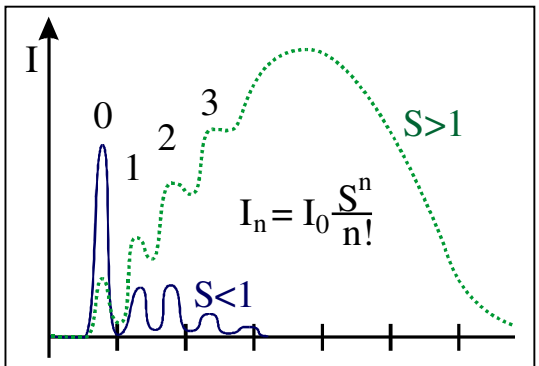

Figure 3 – Emission spectrum with phonon sidebands. S corresponds to the Hyang-Rhys number.

2. Experimental procedure

a. Prepare the experimental setup: perform a calibration curve, obtain a measurement of the energy- and time-resolved spectra of the diodes employed in the experiment.
b. Obtain time-resolved spectra of the samples (ruby, YAG:Cr and sphalerite), in the wavelength interval between 0.35 μm and 0.85 μm.
c. Perform time-resolved spectral for the YAG:Cr and ruby samples in the wavelength range 0.6 μm ≤ λ ≤ 0.8 μm.
d. Repeat measurements of c) with the samples in liquid nitrogen.

3. How to prepare the report:

The report should contain the following sections:
1. Abstract,
2. Theoretical introduction,

3. Description of the samples and experimental setup,
4. Results and their analysis,
5. Summary and conclusions, based on the measured data.

Please note that:

1. The abstract should consist of a few sentences containing the description of the experiment and its main results,
2. All equations should be justified, and their origins explained,
3. In the description of the experimental setup, the characterization of the monochromator, as well as the time- and energy-resolved spectra of the diodes used should be presented (e.g. lighting and extinction times).
4. The results of the experiment are time-resolved luminescence spectra, which should also be presented as a series of energy-resolved spectra at different times after the excitation is turned off. Because the intensity of the transition decays as an exponential function, the time scales picked for the different energy-resolved $I(\lambda)$ spectra should be in the logarithmic scale.
   To analyze the luminescence spectra of ZnS:Cu, ruby, and YAG:Cr, it is necessary to first identify each material's main emission line. In the case of ruby and YAG:Cr, the electronic transitions should be analyzed through the Tanabe-Sugano diagram by identifying consecutive phonon transitions. Their relative intensities should be calculated for each $I(\lambda)$ spectrum. Results at different temperatures should be compared. For sphalerite, the donor-acceptor recombination time should be determined for each one of the visible emission bands.
5. Provide a physical explanation for the observed results.
6. When preparing the presentation, please remember that figures must be correctly labelled (e.g. Fig. 1, 2, 3, etc...), and should be referred by their labels (NOT by "see the figure below"). Figures should be accompanied by a description below the figure. Tables (if any) should also be numbered. However, differently from figures, tables are titled (i.e. the description is atop the table, not below it). Whenever a reference is used, or results from other authors are cited, they should follow with the appropriate reference between brackets (e.g. [1]). The referencing style is up to the author of the report, but should be consistent.

4. Further reading

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 - „Wstęp do fizyki ciała stałego."
4. T. S. Moss - „Optical properties of semiconductors"
5. J. I. Pankove - „Zjawiska optyczne w półprzewodnikach."
6. F. A. Cotton - „Teoria grup. Zastosowanie w chemii."
7. A. Gołębiowski - „Chemia kwantowa związków nieorganicznych."
8. J. Houghton, S. D. Smith - „Fizyka podczerwieni."
9. G. F. Imbush - „Energy levels and transitions of transition metal ions in solids"
10. T. Stacewicz, A. Kotlicki - 'Elektronika w laboratorium naukowym"
11. Encyklopedia fizyki, Wikipedia - hasła monochromator, oscyloskop.

K.K., R.S., B.C., 08 IV 2023

Appendix: **Labview**

The program used for measurements is prepared in LabVIEW (***Lab****oratory* ***V****irtual* ***I****nstrument* ***E****ngineering* ***W****orkbench*). For its use, the program (rubyn.vi) should first be opened and ran (ctrl + r). Once the script is running, measurements are possible.

1 – To certify that the program is running, verify if the "oscilloscope wavefunction" window shows the same data shown in the screen of the oscilloscope.
2 – The LabVIEW program registers the spectrum visible at the oscilloscope at different positions of the stepper motor, which is mechanically coupled to the monochromator. It is important to register the initial point of each measurement (by looking at the scale in the monochromator). This will be the first measured point. Consecutive measurement points will be at fixed angular displacements of the motor ("step size"). The measurement will be repeated the number of times defined in the "number of steps" field. For example, a measurement of step size 10 and number of steps 100 will measure 100 points, 10 steps apart from each other. **Please refer to the encyclopedia of your choice to assess how a stepper motor works**.
3 – The data is recorded as a series of values for each position of the motor, representing the measured voltage by the detector at equally distant time intervals. The time scale is defined on the oscilloscope, and should be noted down prior to measurements.
4 – "number of averages", or "averaging" defines how many spectra are measured at the same position of the stepper before moving to the next point.
5 – Once all parameters are set, press the "start measurement" button to start measuring.
6 – Do not forget to calibrate the monochromator scale before all measurements. Also, certify that the calibration obtained is valid (for example, ensure that all measurements start at the same point).