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Facultad de Ciencias

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Trabajo Fin de Grado

Luminescent response study of ionic crystals used in dosimetry

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Fecha de entrega

Agradecimientos

Incluir los agradecimientos, si procede.

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Resumen

Escriba aquí un resumen de la memoria en castellano que contenga entre 100 y 300 palabras. Las palabras clave serán entre 3 y 6.

Palabras clave: palabra clave 1; palabra clave 2; palabra clave 3; palabra clave 4

Abstract

Insert here the abstract of the report with an extension between 100 and 300 words.

Keywords: keyword1; keyword2; keyword3; keyword4

CAPÍTULO 1

Introduction

As a bystander, one may pass life without thinking of the things that surrounds us. One may have had the misfortune of entering on an MRI, or the responsability to carry a dosimeter in a nuclear plant, and stepped out the room as it is. Life can go on unquestioned, and one may get out of that PET scan without thinking of the source of that awful noise.

There's beauty in the mundane, and the world is full of wonders. The universe is a complex system of interactions, and we know a very small part of it. We are surrounded by radiation, and we are constantly exposed to it. It is a natural phenomenon that has been present since the beginning of time, and it is an integral part of our existence. There are answers for those who wonder, and this work is a very small step towards it.

Luminescence is a phenomenon familiar to us; and goes through our lives like a commercial break. We see it in the glow of a firefly, the sparkle of a diamond, or the light emitted by a fluorescent lamp. In a nutshell, it is a process where energy is absorbed and re-emitted as light, leaving a trail behind, and can be triggered by various stimuli, like heat, light or radiation. This broad notion is the reason why the study of luminescence has practical uses in many fields. One of those fields of use is the detection of ionizing radiation, a field generally known as "dosimetry". The amount of radiation absorbed by a material can be measured by the amount of light emitted when the material is stimulated, and this is the basis for many dosimetry techniques. These luminescence-based methods for detecting ionizing radiation have played a central role in radiation research since the earliest discoveries of radiation, as they exploit the ability of specific materials to emit light when exposed to ionizing radiation, to detect and quantify the radiation received, further expanding the knowledge its efect.

One of the most commonly used materials in this context is lithium fluoride doped with magnesium and titanium (LiF:Mg,Ti). This material exhibits thermoluminescence, a phenomenon where after irradiation, its internal structure captures a memory of the event, in the form of trapped electrons. Upon heating, these trapped charges are released; recombining and emitting photons in the process. The resulting light —that we know to be called luminescence—, if recorded as a function of temperature, produces what is called a thermoluminescence (TL) glow curve.

But knowing that LiF:Mg, Ti emits light when heated is only the beginning. The real challenge lies in understanding it. Interpreting it. The glow curve, with its peaks and valleys, is more than a passive result. It is a message from within the material, shaped by the dance of the electrons accross the imperfections of the lattice, and it tells a story —if we know how to read it.

To make sense of that story, one must model it. That is, to simulate the physical processes that give rise to the obersed glow, and to see whether our mathematical model truly mirror nature. Can we, with a set of parameters and approximations, recreate the fingerprint of radiation? Can we extract from that curve a clear image of the processes within?

This is where this work begins. At the heart of this discourse lies the attempt to reproduce the TL glow curve of LiF:Mg, Ti through computational modeling. This effort leans on the shoulders of many brilliant scientists with an insatiable hunger for one of the many misteries of the universe, one where electrons takes us across energy barriers, where recombination is probabilistic, and where heat becomes the catalyst of understanding.

But even the best models are incomplete. Many assume constant parameters —fixed frequency factors and activation energies, unchanged by temperature or entropy. Reality, as often, lies in a space in between. In these pages, it will be investigated what happens when we let these parameters breathe. By introducing temperature-dependent frequency factors, we will investigate how this modification reshapes the predicted glow curve. Is the model improved? Do we get closer to the experimental results? Can it go beyond known data and predict a hypothetical future case?

Ultimately, the motivation is simple: to understand. To refine our lens on thermoluminescence; to bridge the hap between theory and experience, and to contribute, even in the smallest way, to the slow unraveling of the invisible questions that shape our everyday lives.

CAPÍTULO 2

Objectives

CAPÍTULO 3

Theoretical framework

3.1. The mathematical model

To describe the thermoluminescent response of a semicoductor, we can use a mathematical model based on the trapping and releasing of charge carriers in the accesible energy levels of the material.

Let us first consider the case of an arbitrary semicoductor without impurities. The energy levels of the conduction band and the valence band are separated by a bandgap E_g, and can be obtained with Schrodinger's equation that is under the influence of a periodic potential:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\ \psi(\vec{r}), \tag{3.1}$$

The periodicity of the potential $V(\vec{r})$ for any lattice vector $\vec{R}$ allows the Bloch's theorem to apply, and so it gives rise to the formation of a band structure, composed by the conduction band, which is typically fully occupied at absolute zero temperature, and the valence band, which is in turn typically empty -or rather, we can consider it filled with holes (h^+), or "positively charged electrons". The bandgap E_g is then defined as the energy difference between the top of the valence band and the bottom of the conduction band, and for a perfect crystal, no energy states are allowed in that region. This can be clearly seen if we take into account the density of available states, $D(E)$, which is a function of the Fermi-Dirac distribution $f(E)$ for a certain temperature T. This function gives the occupancy of any energy level E, and can be expressed as:

$$f(E) = \frac{1}{e^{\frac{E-E_f}{k_B T}} + 1}, \tag{3.2}$$

Where E_f is the Fermi Level, and k_B is the Boltzmann constant. If the system is in equilibrium, and we set the case of $T = 0K$, the occupancy function $f(E)$ will be equal

to 1 for all energy levels below the Fermi level, and 0 for all energy levels above it. This means that the occupancy function will be a step function, with a discontinuity at the Fermi level, and so we can see that there are no available states in the bandgap region.

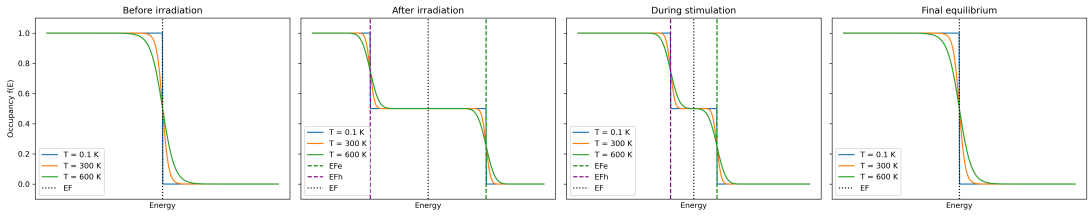

Figura 3.1: Fermi-Dirac distribution for a semicoductor that is irradiated.

The introduction of impurities or defects however, break the periodicity of the lattice, and create localized energy levels inside this "forbidden region". These levels can be thought of as traps for electrons if we are situated above the fermi level, and traps of holes if we are situated below. When this material is irradiated, electrons from the valence band can be excited to the conduction band, creating an electron-hole pair; and so changing the shape of the occupancy function. Once excited, both electrons and holes get "trapped" in these localized energy levels, and the excitation of these pairs into equilibrium will result in the emission of energy. In Figure 3.1 we can see a broad description of the perturbation of the system from its equilibrium state due to the irradiation, and the return of the system to equilibrium during either thermal stimulation or optical stimulation. If said relaxation processes are radiative, TL and OSL result.

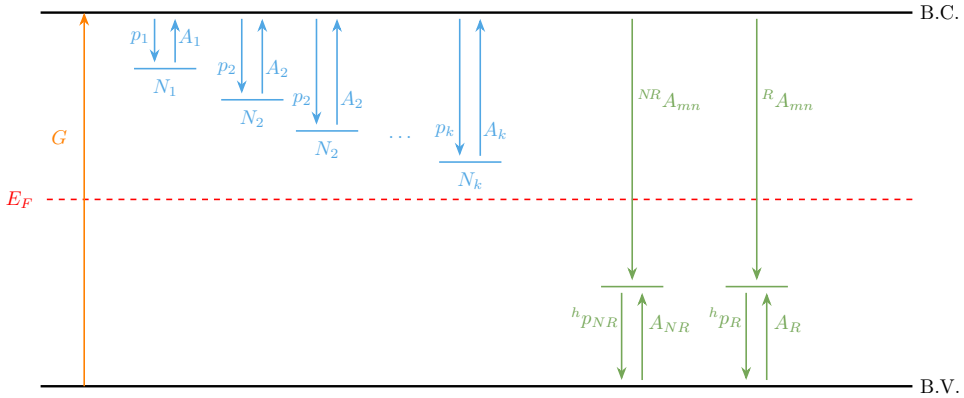

Figura 3.2: Schematic representation of the theoretical model.

And so, we can see a schematic representation of our theoretical model in Figure 3.2. Situating the energy in the Y axis, the focus is set in the energy gap of our material. Drawn as a blue or green horizontal line are the energy traps; in blue above the Fermi level there are electron traps, and in green there are hole traps or recombination centers. The vertical arrows describe available transitions; the ones pointing upwards represent an excitation process, and the ones pointing downwards represent a relaxation process.

Mathematically, we can describe these processes with a set of differential equations that take into account the rate of change of the number of electrons and holes in the bands and traps. This set will depend on the properties of the material, and the luminescence response we are trying to model. For an arbitrary system, we can write the following set

of equations that describe the rate of change of the number of electrons and holes in the conduction band n_c, the valence band n_v:

$$\frac{dn_c}{dt} = G - \left[\sum_i \frac{dn_i}{dt}\right] \cdot n_c - \left[\sum_{j=R,NR} {}^{i}A_{mn} \cdot m_j\right] \cdot n_c \tag{3.3}$$

$$\frac{dn_i}{dt} = -p_i \cdot n_i + A_i \cdot [N_i - n_i] \tag{3.4}$$

$$\frac{dm_j}{dt} = -{}^{h}p_j \cdot m_j + A_j \cdot [M_j - m_j] \cdot n_v - {}^{i}A_{mn} \cdot m_j \cdot n_c \tag{3.5}$$

$$\frac{dn_v}{dt} = G - \sum_{j=R,NR} \left[-{}^{h}p_j \cdot m_j + A_j \cdot [M_j - mj] \cdot n_v\right] \tag{3.6}$$

Where every term is defined as follows:

- G: electron-hole pairs generated by the radiation [$\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$]
- n_c: electron concentration in the conduction band [cm^{-3}]
- n_v: electron concentration in the valence band [cm^{-3}]
- n_i: electron concentration in trap i [cm^{-3}]
- m_j: hole concentration in the recombination center j [cm^{-3}]
- N_i: total density of electron trapping centres in trap i [cm^{-3}]
- M_j: total density of recombination centers [cm^{-3}]
- p_i: electron release probability factor for trap i [s^{-1}]
- ${}^{h}p_j$: hole release probability factor for recombination center j [s^{-1}]
- A_i: electron trapping probability factor for trap i [$\mathrm{cm}^3\ \mathrm{s}^{-1}$]
- ${}^{i}A_{mn}$: recombination probability factor for recombination center j [$\mathrm{cm}^3\ \mathrm{s}^{-1}$]

Equation 3.3 describes the change rate of electron concentrations in the conduction band. To interpret this equation, we can see that to the electron-hole pairs generated by the radiation (G), there are two terms substracted. The first one correlates to the electrons that leave the continuum levels of the conduction band and get trapped in the discrete levels of the material —a process described by 3.4, that will have a further discussion in section 3.2—, and the second one answers to the electrons in the conduction band that recombine with holes with a radiative (R) or non-radiative (NR) process. It is easy to see that this second term corresponds to the third term of 3.5.

The change rate of electron concentrations in the valence band is shown in 3.6, and it follows a similar logic. This time however, we only take into account the terms multiplied by the electron density in the valence band (n_v) seen in equation 3.5; one that represents the holes leaving the continuum to get trapped in the recombination centers, and another that accounts for the addition of electrons that are released from the recombination centers and recombine with the holes in the valence band. The terms described correspond to Equations 3.4 and 3.5 describe the total change rate of electrons and holes in the discrete levels of the material. The signs of the terms in these equations follow the convention that

we are set in the conduction band, and so any electron that leaves the conduction band is represented with a negative term, and any electron that enters is represented with a positive term.

To carry out a numerical simulation of the process, we will need to solve the set of differential equations 3.3 – 3.6 using RKF-45 method, which is a Runge-Kutta method of order 4 and 5. This method will obtain the charge concentration in all traps and recombination centers at an instant of time. The solving of this set of equations will be done for the three phases required to obtain the TL glow curve. To do this, the intrinsic and kinetic parameters are kept constant, varying the external conditions of the system such as temperature and electron-hole pair generation rate.

The first phase is *irradiation*, where the material is exposed to ionizing radiation. It begins with all levels initially empty $[n_c(0) = n_v(0) = n_i(0) = m_j(0) = 0]$, and the electron-hole pairs generated as a result will have a constant value as a function of time ($G = 1000$ cm^{-3} s^{-1}). The temperature is set to a constant $T = 25$ °C and the filling process takes one hour (3600 seconds). The second phase is *relaxation*, where the material is left undisturbed at a constant temperature for a defined period of time. Taking as initial values the final values of the irradiation phase, the temperature is kept constant at $T = 25$ °C, and the electron-hole pairs generation rate is set to $G = 0$ cm^{-3} s^{-1}. The relaxation process is set for one week (604,800 seconds). Finally, the third phase is *heating*, where the material is taken from an initial temperature T_0 to a final temperature at a constant linear heating rate. The numerical resolution of the set equations is similar to the previous phases, but now with the temperature varying linearly with the expression:

$$T(t) = T_0 + \beta \cdot t \tag{3.7}$$

Where the heating rate is set to $\beta = 1$ °C s^{-1}. The electron-hole pairs generation rate is set to $G = 0$ cm^{-3} s^{-1}, and the charge concentration values are taken from the final values of the relaxation phase. The heating process is set to last 400 seconds. The results after the numerical resolution of the set of equations will be the charge concentration values for every instant of time throughout the whole heating cycle $[n_c(t), n_v(t), n_i(t), m_j(t)]$. It is in this phase when the luminescent emission occurs, and so the intensity of the emmited light can be estimated in relation to the radiative recombination of electron-hole pairs. We can give the expression for the intensity of the emitted light as it follows:

$$I(t) = -\frac{dm}{dt} \approx {}^{R}A_{mn} \cdot m_R \cdot n_c \tag{3.8}$$

Representing this intensity as a function of time will be the objective of the simulations, as it is the key to understand the thermoluminescent response of the $LiF : Mg, Ti$ after being irradiated.

3.2. The frequency factor

As introduced in Section 3.1, there is a greater discussion to be had about the releasing probability of electrons and holes, as it determines in great part the electron-hole pairs available to recombine. If we consider that after being irradiated, the material will release its carriers through *thermal excitation*, an electron trapped in a lattice defect with energy

E_t and temperature T will have a probability of being released that follows Arrhenius equation. The probability per second that the electron will be thermally excited into the conduction band is given by:

$$p = s \cdot e^{-\frac{E_t}{k_B T}} \tag{3.9}$$

Where s is known as the *frequency factor*. It can be interpreted as the "attempt to escape" frequency, as it is a measure of the number of times per second that energy is absorbed from phonons in the lattice. The exponential that follows is the probability that the energy absorbed is enough to cause a transition from the localized state to the conduction band.

The frequency factor is a very important parameter in the study of thermoluminescence, as it determines the rate at which electrons are released from traps. It is a function of the material properties, as shown in its definition:

$$s = \nu_{ph} \cdot K \cdot e^{\frac{\Delta S}{k_B}} \tag{3.10}$$

Where ν_{ph} is the lattice phonon vibration frequency and K is the transition probability constant. Typically, one can expect $s \sim 10^{12} - 10^{14}$ s^{-1}, which is consistent with the values of ν for most solids. The term $e^{\Delta S/k_B}$ is a correction factor that accounts for the entropy change associated with the transition from the localized state to the conduction band.

From equation 3.10 we see that the frequency factor has an exponential dependency with the entropy change. This, taking the Quantum Statistical Mechanics theory [3], does not align with the invariance of said factor with temperature, as entropy, with its own definition, should vary when temperature does. While a rigorous proof of the overall temperature dependence of the frequency factor is beyond the scope of this work, one model is proposed to provide an approximate perspective on how this dependency could influence the resulting TL glow curve.

At first glance, the simplest model was considered, where the entropy would be linear with the temperature ($\Delta S \propto T$). This theory was quickly discarded as would make the entropy factor increase exponentially with the temperature ($s \propto e^T$), and so the probability of excitation would tend to infinity in a very short range of temperature increase.

To solve this issue, a more refined model was considered, where the entropy would now be logarithmically dependent on the temperature ($\Delta S \propto \ln(T)$). The constant of the proportionality could be called α, and so the resulting expression of the frequency factor can be written as:

$$s = \nu_{ph} \cdot K \cdot T^{\alpha/k_B} \tag{3.11}$$

It is clear now that a softer dependency with the temperature is achieved, and the previous problem of the entropy factor tending to infinity is solved. The value of α can be adjusted to keep the entropy contribution at a realistic magnitude —typically we have $\Delta S \sim 1$–$3\ k_B$ over the glow curve temperature range—. For that reason, we have selected a value of:

$$\alpha = \frac{1.5\ k_B}{ln(300)} \approx 0.26\ k_B \tag{3.12}$$

This choice ensures that the frequency factor remains within a reasonable range across the temperature spectrum of interest, and yields TL glow curves that are consistent with experimental observations of LiF:Mg,Ti materials.

3.3. About LiF:Mg,Ti

Lithium fluoride (LiF) is a crystalline material that has been widely used in radiation dosimetry due to its favorable properties. It first appeared as a thermoluminescent dosimetry material in the 1950's, and since then, it has been extensively studied in the field of radiation detection. The material is composed of lithium (Li) and fluor (F) atoms, forming a crystal lattice structure of a face-centered cubic (FCC) type. Without any impurities, LiF is a semiconductor, with a bandgap of approximately 14 eV, which makes it an excellent insulator at room temperature.

To enhance the properties for radiation detection, LiF is often doped with magnesium (Mg) and titanium (Ti) ions, and sold commercially as TLD-100 [1]. The doping process introduces defects in the crystal lattice, creating energy levels within the bandgap. These defects play a crucial role in trapping and releasing charge carriers, which are responsible for the thermoluminescent response of the material. This process is known as thermoluminescence (TL), where the trapped electrons are released upon heating, resulting in the emission of light. The intensity of this emitted light is proportional to the amount of radiation absorbed by the material, making it a valuable tool for dosimetry.

The TL response of LiF:Mg,Ti is characterized by a glow curve, which is a plot of the intensity of emitted light as a function of temperature. The glow curve typically exhibits several peaks, each corresponding to different trapping levels in the material. The position and shape of these peaks can provide valuable information about the trapping and recombination processes occurring in the material, and they are key to understanding the thermoluminescent response of LiF:Mg,Ti.

CAPÍTULO 4

Simulations

4.1. Materials used for simulations

The materials used for this work are all the digital tools required for the simulation of the behaviour of our material of choice. In our case, the project was made using *Python* in a Jupyter Notebook. The programs written are available on the GitHub repository called `TFG_MartadelaRosa`.

The libraries used for the simulations are:

- `numpy`: This library is used for numerical calculations and array manipulations.
- `matplotlib`: This library is used for plotting graphs and visualizing data.
- `pandas`: This library is used for data manipulation and analysis, providing data structures like DataFrames.
- `scipy`: This library is used for scientific computing and includes functions for optimization, integration, interpolation, and more. In particular to solve the differential equations that describe the kinetics of the TL process.

4.2. Simulations

To compute a simulation of the TL process described in Section 3.1, after defining the parameters of the model, we need to solve the differential equations that describe the kinetics of the TL process. The equations are solved using the `odeint` function from the `scipy.integrate` library, which is a powerful tool for solving ordinary differential equations. The function takes as input the system of equations, the initial conditions, and the time points at which we want to evaluate the solution. The output is an array containing the values of the variables at each time point, which is then saved to their corresponding

variables, used to plot the results. They are brought to life using the `matplotlib` library, and for every resolution of the differential equations, we will present three graphs as the result.

Conclusiones

En este trabajo ...

Conclusions

In this work ...

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Anexo: Ejemplo para introducir código Matlab

```
%% 3-D Plots
% Three-dimensional plots typically display a surface
% defined by a function in two variables, z = f(x,y) .
%%
% To evaluate z, first create a set of (x,y) points
% over the domain of the function using meshgrid.
    [X,Y] = meshgrid(-2:.2:2);
    Z = X .* exp(-X.^2 - Y.^2);
%%
% Then, create a surface plot.
    surf(X,Y,Z)
%%
% Both the surf function and its companion mesh display
% surfaces in three dimensions. surf displays both the
% connecting lines and the faces of the surface in color.
% Mesh produces wireframe surfaces that color only the
%lines connecting the defining points.
```

Anexo: Ejemplo para introducir código ISE

```
1  library IEEE;
2                 use IEEE.STD_LOGIC_1164.ALL;
3                 use IEEE.STD_LOGIC_ARITH.ALL;
4                 use IEEE.STD_LOGIC_UNSIGNED.ALL;
5  -- Uncomment the following library declaration if
6  -- instantiating  any Xilinx primitive in this code.
7  -- library UNISIM;
8  -- use UNISIM.VComponents.all;
9
10 entity counter is
11     Port ( CLOCK : in  STD_LOGIC;
12     DIRECTION :    in  STD_LOGIC;
13     COUNT_OUT :    out STD_LOGIC_VECTOR (3 downto 0));
14 end counter;
15
16 architecture Behavioral of counter is
17 signal count_int : std_logic_vector(3 downto 0) := "0000";
18 begin
19 process (CLOCK)
20 begin
21     if CLOCK='1' and CLOCK'event then
22         if DIRECTION='1' then
23             count_int <= count_int + 1;
24         else
25             count_int <= count_int - 1;
26         end if;
27     end if;
28 end process;
29 COUNT_OUT <= count_int;
30 end Behavioral;
```