

VIBRONIC FINGERPRINTS OF INORGANIC PHOSPHOR MATERIALS FROM FIRST PRINCIPLES

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ABSTRACT

This thesis explores the vibronic properties of Eu-doped phosphor materials, which are essential components in modern lighting technologies, particularly in phosphor-converted white light-emitting diodes (LEDs). Using first-principles simulations, the work focuses on understanding and modeling the luminescence lineshapes of these materials through a generalized Huang-Rhys model, fed by density functional theory calculations. The computational methodology addresses key challenges such as describing long-range atomic displacements induced by electronic transitions in computationally tractable supercell sizes, and simultaneously capturing the coupling with long-wavelength phonons and defect-localized phonons using an embedding approach for the interatomic force constant matrix.

This research introduces the “Lumabi” Python package, a tool designed to automate the computation of phonon-resolved luminescence spectra in defect systems using the ABINIT density functional theory (DFT) software.

A significant portion of the study is dedicated to Eu-doped UCr_4C_4 -type phosphors, such as $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ and $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$. Detailed analyses of atomic displacements within the 1D cation channel provide insights into their emission spectra. The coupling of these displacements with low-frequency phonon modes was identified as a common cause of the characteristic narrow emission lineshapes observed in these materials.

Moreover, the theoretical methodology was applied to identify defect centers responsible for luminescence via their vibronic fingerprints. In the red-emitting phosphor $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$, the two non-equivalent Sr sites were distinguished based on their respective luminescence spectra and comparisons with experimental data. Similarly, in the green-emitting phosphor $\beta\text{-SiAlON}:\text{Eu}^{2+}$, simulations confirmed the Eu interstitial site in the host structure to be the emitting one.

We hope to provide valuable insights and tools aimed at deepening the understanding of the material-property relationships in Eu-doped phosphors.

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PUBLICATIONS

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- Bouquiaux, J., Poncé, S., Jia, Y., Miglio, A., Mikami, M., & Gonze, X.. A First-Principles Explanation of the Luminescent Line Shape of $\text{SrLiAl}_3\text{N}_4: \text{Eu}^{2+}$ Phosphor for Light-Emitting Diode Applications, [Chemistry of Materials](#) **35**, 5353-5361 (2023)
- Bouquiaux, J. *et al.* Simulating complex phonon-resolved luminescence spectra of defects made simple with the "Lumabi" software. *In preparation.*
- Bouquiaux, J. *et al.* A first-principles confirmation of the Eu location in low-z $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}:\text{Eu}^{2+}$ green phosphor through vibronic analysis. *In preparation.*

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LIST OF ABBREVIATIONS

ASR	Acoustic Sum Rule
CCM	Configuration Coordinate Model
CIE	Commission Internationale de l'Éclairage
DDB	Derivative DataBase
DFPT	Density Functional Perturbation Theory
DFT	Density Functional Theory
DOS	Density of States
FC	Franck-Condon
FWHM	Full Width at Half Maximum
GGA	Generalized Gradient Approximation
HR	Huang-Rhys
IFC	Interatomic Force Constants
IPR	Inverse Participation Ratio
LDA	Local Density Approximation
LED	Light Emitting Diode
PAW	Projector Augmented-Wave
PBE	Perdew-Burke-Ernzerhof (a type of GGA functional)
PL	Photoluminescence
PLE	Photoluminescence Excitation
PSB	Phonon Sideband
QHA	Quasi-Harmonic Approximation
SCF	Self-Consistent Field
UV	Ultraviolet
WLED	White Light Emitting Diode
ZPL	Zero-Phonon Line

INTRODUCTION

LIGHT-EMITTING DIODES AND PHOSPHOR MATERIALS

Environmental issues urge the need for energy saving in every sectors of society. Improving the energy efficiency of common technologies is essential for reducing CO₂ emissions. One sector where significant gains have been made is lighting, by replacing old incandescent lamps with more efficient light sources such as white-light emitting diodes (WLEDs), see figure 1. WLEDs have become a new light source for lighting and backlight displays in the 21st century. Predictions suggest that by 2035, LED lighting will account for 84% of all lighting installations. As of 2020, LED lighting accounted for only about 35%, indicating significant potential for growth [1]. In the U.S., the use of LED lighting saves approximately 185 TWh of energy per year compared to conventional lighting technologies, and it has the potential to save up to 500 TWh of energy per year by 2035 [2]. In terms of CO₂ savings, this equates to an estimated saving of 79 MMT (million metric tons) in 2020 and 154 MMT in 2035, compared to a scenario where LED technology never entered the lighting market. In 2020, total CO₂ emissions due to lighting in the United States were estimated to be approximately 208 MMT. A life cycle assessment was used to estimate the breakdown of the total environmental impact of LEDs. Approximately 85% of the impact occurs during the use phase, where efficiency and lifespan are the key contributing factors. The manufacturing and end-of-life phases account for most of the remaining impact, while shipping contributes only 1 to 2% of the total environmental impact [2].

LEDs possess substantial advantages, including small size (suitable for miniaturized application equipment), low power consumption (one-eighth to one-tenth that of ordinary light bulbs and half that of fluorescent lamps), long lifetime (up to 100,000 hours), low heat radiation, and good response speed (high-frequency operation).

As shown in the lower-right part of figure 2, a monochromatic light-emitting diode consists of several layers: an n-type layer with an electron excess, and a p-type layer with a hole excess. Between them is an active layer, to which the negative electrons and the positive holes are

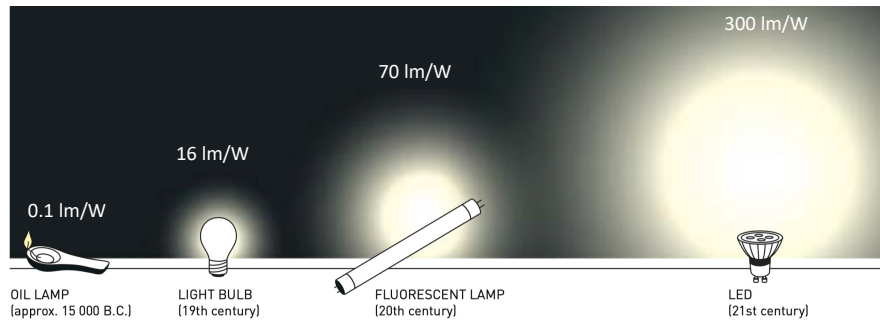


Figure 1: Graphical representation of the historical trend in increasing the luminous efficacy over the years with new lighting technologies. Adapted from [3].

driven when an electric voltage is applied to the semiconductor. The recombination of the electrons and holes creates photons and light is created with a wavelength that is controlled by the band gap of the semiconductor.

The development of the blue light-emitting diode was a major breakthrough that revolutionized modern lighting. In 2014, Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura were awarded the Nobel Prize in Physics for their pioneering work on efficient blue LEDs [3]. This invention was crucial because, while red and green LEDs had existed for years, the creation of blue light was essential to generate white light.

Indeed, eco-efficient WLEDs generally rely on one or more phosphor materials to convert the ultraviolet (UV) or blue emission from a LED chip into a desired wavelength emission spectrum (see figure 2). Phosphors, or light-conversion materials, are the second key components of WLEDs. They are typically made of a host material (e.g. $\text{Y}_3\text{Al}_5\text{O}_{12}$) doped with an activator (e.g. Ce^{3+}), which emits light. The characteristics of the emitted light is influenced by the host crystal structure, the choice of the activator, and its direct chemical environment. The various compositions of host materials and activators have led to thousands of possible phosphor materials, each with unique photoluminescent properties such as quantum efficiency, emission wavelength, thermal stability, or shape of the emission spectra. Understanding the link between the material and the end property (here the photoluminescence) is crucial, first from a pure curious academic point of view, but

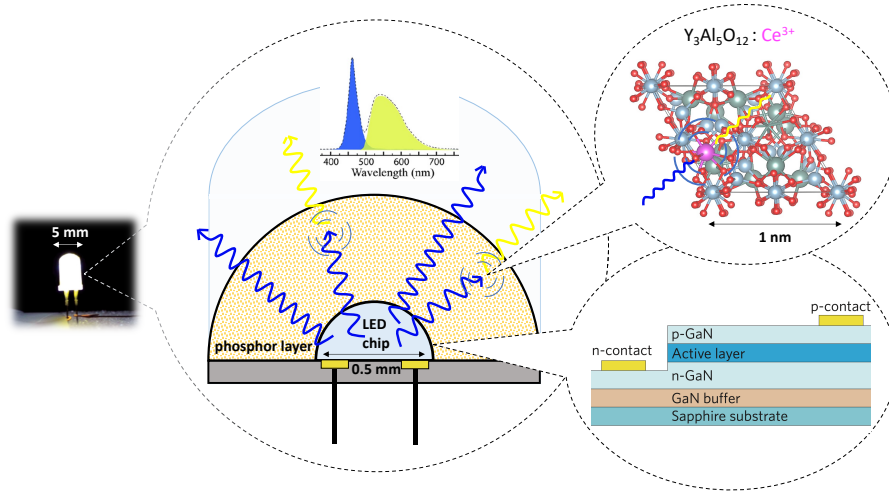


Figure 2: Schematic representation of a phosphor-converted white-light emitting diodes device.

also from an engineering point of view, as it allows to search and design more efficiently new phosphors.

As an example of such quest for more performant materials, we can already mention the large effort put in the last decade on discovering phosphors with narrow emission bandwidths to improve the color purity of backlighting LED devices and to avoid energy waste in the near-infrared region, which is not visible to the human eye. This search led to the development of the now so-called UCr_4C_4 phosphors, for which the material-property relationship will be discussed in depth in this manuscript.

COMPUTATIONS IN MATERIALS SCIENCES

For decades, the development of efficient phosphor materials has primarily relied on empirical methods, such as simple models, trial and error, and intuition. While this process can be time-consuming, it has nevertheless been instrumental in many significant advances. A famous example is Thomas Edison's search for an efficient light bulb filament, during which he tested and evaluated over 3000 filaments. Nikola Tesla remarked : " *His method was inefficient in the extreme, for an immense ground had to be covered to get anything at all unless blind chance intervened and, at first, I was almost sorry to witness of his doings, knowing that just a little theory and calculation would have saved him 90 per cent of*

the labor. But he had a veritable contempt for book learning and mathematical knowledge, trusting himself entirely to his inventor's instinct and practical American sense. In view of this, the truly prodigious amount of his actual accomplishments is little short of a miracle" [4].

In this context, employing computational techniques that are both time-efficient and sufficiently accurate to be predictive presents an appealing way to accelerate the understanding and discovery of efficient luminescent materials. However, simulations should complement, rather than replace, experimental work.

Indeed, first, the simulation of the full complexity of real-life materials is, and will likely remain for long, beyond reach. Simulations always employ a model of the problem to be solved. In our case, we know that photo-luminescent properties in phosphors arise from point defects. Thus, one approach is to model an infinite perfect crystal with an inserted point defect. This is an idealized view since real materials contain other defects (which might also be luminescent) that are ignored in the simulation. For example, in this work, we overlook grain boundaries, defect-defect interactions, or the effects of optical center killers. This constitutes the first type of approximation in modeling: approximating the physical system of interest.

Secondly, a comprehensive understanding of material properties requires an atomistic description, achievable only through quantum mechanics. Light absorption and emission, due to electron excitation and de-excitation, are purely quantum mechanical effects. Unfortunately, the Schrödinger equation, which must be solved for realistic materials, scales very poorly with the number of particles due to the complex many-body wavefunctions that describe the system. Even advancements in the micro-electronic industry, which provided exponential growth in computational power (Moore's law), are insufficient for computing the properties of molecules with more than a few atoms *ab initio* without relying on approximations.

A significant theoretical advancement occurred due to the foundational work of Kohn, Hohenberg, and Sham, who developed a series of theorems and approximations that enabled a quantum theory of solids and molecules, bypassing the complex wavefunction description and instead using the much simpler charge density. These developments led to Density Functional Theory (DFT) [5], currently the most widely used *ab initio* technique. While exact in theory, practical DFT computations rely on approximation schemes. This represents the second type of approximation in modeling: approximating the mathematical

description (here the many-body Schrödinger equation) to make the problem computationally tractable.

While computational techniques offer valuable insights into material properties, they are not without limitations. Both experimental and computational approaches are essential for advancing our understanding of phosphor materials. Experiments provides the empirical ground and validation that computational methods alone cannot achieve, and the two methodologies must work in pair to drive progress.

OBJECTIVES OF THIS WORK

Characterizing the luminescent properties of materials is crucial for numerous applications, particularly in the development of white light-emitting diodes. This capability not only enhances our understanding of the underlying physics of experimentally known materials but also allows for the prediction of a material’s suitability for specific applications before experimental validation.

In the field of luminescent materials, confidently identifying the optical centers responsible for luminescence is often challenging yet essential for optimizing material properties. Without this knowledge, material performance may be unpredictable, limiting further advancements. One effective method for this identification involves analyzing the “vibronic” peaks in the experimental luminescent spectrum and comparing them with simulation results. These vibronic peaks, that are a signature of the lattice response to a radiative electronic transition, are highly sensitive to the microscopic environment of the defect responsible for luminescence, providing a distinctive fingerprint of the atomic environment.

In the chapter 1 of this manuscript, we begin with a clarification of the terminology and a brief overview of the applications of phosphor materials. This is followed by a phenomenological explanation of the photo-luminescent mechanisms in these materials and the introduction of the Huang-Rhys model. Chapter 2 presents a more rigorous quantum mechanical formalism that, through a series of carefully applied approximations, yields an efficient mathematical framework for modeling the luminescence lineshape of defect centers using the generating function approach. Special attention is given to systematically track these various approximations. Chapter 3 discusses how Density Functional Theory (DFT) is employed in this work to compute the mathematical components of the lineshape equation. Significant efforts were

made during this PhD to develop codes that facilitate the simulation of luminescent material lineshapes, and these developments are detailed in chapter 4 .

Finally, chapters 5 and 6 present practical results on various phosphor materials with a focus on the computation of their luminescence lineshape, and a careful comparison with experimental data when available. More details are given for the $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$, $\text{SrLi}_2\text{Al}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ red-emitting phosphors, and the green-emitting $\beta\text{-SiAlON}:\text{Eu}^{2+}$ phosphor. These three compounds are highly relevant from a technological point of view.

PHOSPHORS MATERIALS

In this first chapter, we start by clarifying the terminology used throughout this manuscript. We explain how phosphor materials play an important role in the performance of white light emitting diode. In particular, we present a family of compounds (UCr_4C_4 structure type) that present interesting narrow emission bands. A first qualitative explanation of the photo-luminescent physical processes is provided, including energy levels in lanthanides, the configuration coordinate model, and the Huang-Rhys model.

1.1 PHOSPHOR TERMINOLOGY

To elucidate the origins of the (sometimes confusing) terminology in this field, it is necessary to begin with a historical explanation.

The term *phosphor* was invented in the early 17th century. According to historical accounts, the alchemist Casciarolo from Bologna, Italy, discovered a bright crystalline stone at the base of a volcano. He heated this stone in a coal oven, anticipating the extraction of a noble metal. Although Casciarolo did not succeed in obtaining any metals, he observed that the sintered stone emitted a red glow in the dark after being exposed to sunlight.

This stone was subsequently named the “Bolognian stone”. The stone in question is believed to have been barite (BaSO_4), with the calcined product being BaS , a known host for phosphor materials [7]. Recent research suggests that copper impurities may

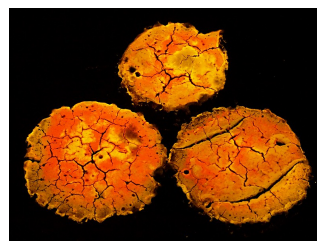


Figure 1.1: A reproduction of the “Bolognian stone” (BaS with Cu impurities) [6].

serve as the emitting center for the persistent luminescence observed in this material [8].

Comparable discoveries were made throughout Europe, leading to the naming of these light-emitting stones as “phosphors,” derived from the Greek term meaning “light bearer.” The term “phosphorescence” emerged subsequently, designating the phenomenon of sustained light emission from a substance after the cessation of exciting radiation. This term is distinct from *fluorescence*, which was introduced by Georges Stokes in 1852 to describe the brief afterglow of the mineral fluorite (CaF_2) following excitation.

The term “luminescence” (originating from the Latin word “lumen,” meaning light), which includes both fluorescence and phosphorescence, was first employed by the German physicist Eilhardt Wiedemann in 1888 [9].

Nowadays, the word luminescence refers to the phenomenon by which the electronic state of a substance is excited by some kind external energy and the excitation energy is given off as light. This light includes the visible region (400 to 700 nm), but also those in the neighboring regions, i.e., the near-ultraviolet and the near-infrared regions.

Currently, the definition of the word *phosphor* itself is not clearly defined and is dependent on the user and context [7]. Still, it is often used to mean inorganic phosphors, usually those in powder form and synthesized to serve practical applications, and can safely be interchanged with the terminology “solid luminescent material”.

In the context of this manuscript, *phosphor* will refer to a crystalline host, where a relatively small amount of impurities (for instance Eu^{2+} substitution) is intentionally introduced to convert light from shorter wavelength to longer wavelength through vibrational energy loss (process called Stokes shift).

It should not be confused the element “phosphorus” (atomic number 15). White phosphorus emits light due to chemiluminescence, a process in which a chemical reaction produces light.

One might also make the distinction between phosphorescence and persistent luminescence (also called long-lasting luminescence or afterglow) that both involve delayed light emission but arise from different mechanisms. Phosphorescence occurs when excited electrons transition through spin-forbidden states, leading to decay times from microseconds to seconds. In contrast, persistent luminescence lasts much longer (minutes to hours) and results from charge carriers trapped in crystal defects. These carriers are gradually released, producing

extended emission, as seen in glow-in-the-dark materials doped with rare-earth ions (e.g., Eu^{2+} , Dy^{3+} , Sm^{3+}).

1.2 PHOSPHOR-CONVERTED WHITE LIGHT EMITTING DIODES

Currently, light-emitting diodes (LEDs) represent a well-developed technology that competes with incandescent and fluorescent lamps. LEDs offer numerous advantages over these traditional lighting sources, including smaller size, longer lifespan, increased robustness, faster switching, and higher efficiency [10]. It is widely accepted that the replacement of incandescent lamps with LED-based alternatives could result in a significant reduction in global electricity consumption, assuming no substantial “rebound” effect [11]. Given that LED chips emit light in a narrow wavelength range, white light cannot be produced directly. However, there are indirect methods to achieve white light :

1. RGB LEDs: Three LEDs chips (red, green and blue) are combined to form a spectral distribution that appears white light to human eye. Although this approach is flexible for display applications, the three narrow-band LEDs may exhibit different behaviors under temperature changes or aging, leading to performance shifts. Feedback electronics with color sensors are typically used to manage this issue, which complicates the overall system.
2. UV diode + RGB phosphors: Here, an LED emitting UV radiation, is used to activate three phosphors (red, green and blue one) to obtain white light, as illustrated on figure 1.2 left.
3. Blue diode + Y/RG phosphors: A blue LED is used to activate a single yellow or a red-green phosphor mixture. The most popular yellow LED phosphor is $\text{YAG}:\text{Ce}^{3+}$, providing a rather cold-white LEDs (figure 1.2 right). A blend of green-red phosphor can be used to yield a warmer white light.
4. UV diode + single mutli-activators phosphor. A UV LED is used to activate a single phosphor material co-doped with multiple activators. The emission wavelength of these different activators should span the whole visible spectrum, with the goal of achieving high color rendering index.

To be used in white LEDs, phosphors must meet a set of technological requirements, as summarized below: [10]:

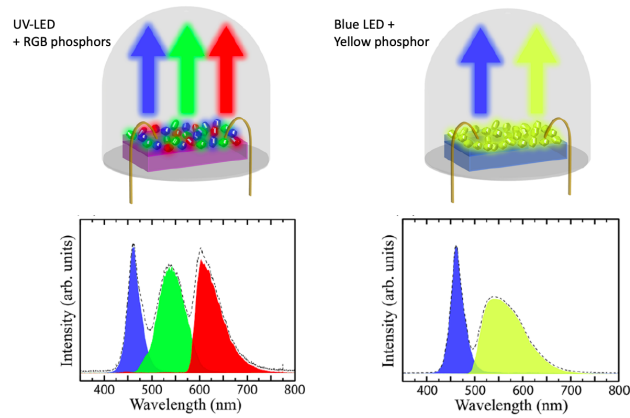


Figure 1.2: Schematic representation of phosphor-based white LEDs based on a UV LED and a mixture of RGB phosphors (left), and a blue LED combined with a yellow phosphor (right), and their corresponding emission spectra. Image adapted from [12].

- An emission spectrum that, in combination with the emission of the other components (LED, other phosphors), leads to a pure white emission with a specific color rendering and color temperature
- An excitation spectrum showing good overlap with the pumping LED and large absorption strength
- An emission spectrum, excitation spectrum and a quantum efficiency that remain unchanged at elevated temperature.
- A quantum efficiency approaching unity, thus maximizing the overall electrical-to-optical conversion efficiency of the entire LED-phosphor package.
- An excellent chemical and temperature stability.
- Absence of emission saturation at high fluxes.

Besides technological requirements, economic and environmental factors are important. Economic considerations involve the cost of phosphors, influenced by synthesis procedures and raw material availability. China holding a lanthanides quasi-monopoly, prices are fluctuating for raw materials and the market is unstable. Phosphors based on lanthanides are often regarded as economically less interesting. Environmental

concerns include the impact of mining, processing, and recycling materials. Lanthanides score poorly on environmental friendliness due to their low concentration in ores, the use of harmful chemicals for separation, and the production of radioactive thorium waste [13].

Overall, finding ways to reduce lanthanide use in phosphors is desirable, though most LED phosphors are still lanthanide-based. Despite these concerns, this work mostly deals with Eu-doped materials but it is our hope that they could be replaced in the future.

Phosphors, in the simplest picture, consist of a host compound doped with impurities. The luminescent properties depend on the intrinsic characteristics of both the host and the dopant, including the type of electronic transition and the details of their interactions. Even minor changes in the dopant-host interaction can significantly impact the phosphor's overall macroscopic physical properties.

Host crystals can have various chemical compositions, such as halides, oxides, sulfides, and nitrides. Activator ions are typically categorized by their position in the periodic table, with lanthanides or 4f elements being very popular. In particular, Eu^{2+} -based phosphors became fruitful candidates compounds in the development of high-performance white light-emitting diodes [14–18], thanks to the nearly-infinite engineering possibilities open by the large sensitivity of the Eu^{2+} emission properties with the structure host. However, transition metals from the 3d series and s^2 ions from the heavy p block are also gaining popularity in the search for lanthanide-free phosphors.

1.3 THE QUEST FOR A NARROW RED-EMITTING PHOSPHOR

While efficient blue, yellow and green phosphors are considered well established today and commercially available, finding an efficient red phosphor is still a critical field of research to further increase the overall luminous efficacy of phosphor converted white LED technology [19]. The main reason for this is the following : The spectral human eye response function (as depicted in grey in figure 1.3, and detailed in appendix C) shows a peak at 557 nm in the green and decay progressively in the red region. Our eyes are less sensitive to red colors. As a result, the part of the emission spectra of a light source that extend in the deep-red and near infra-red region is a waste of spectral power since this spectral region does not overlap with spectral human eye response, leading to an important decrease in the luminous efficacy. Commercial

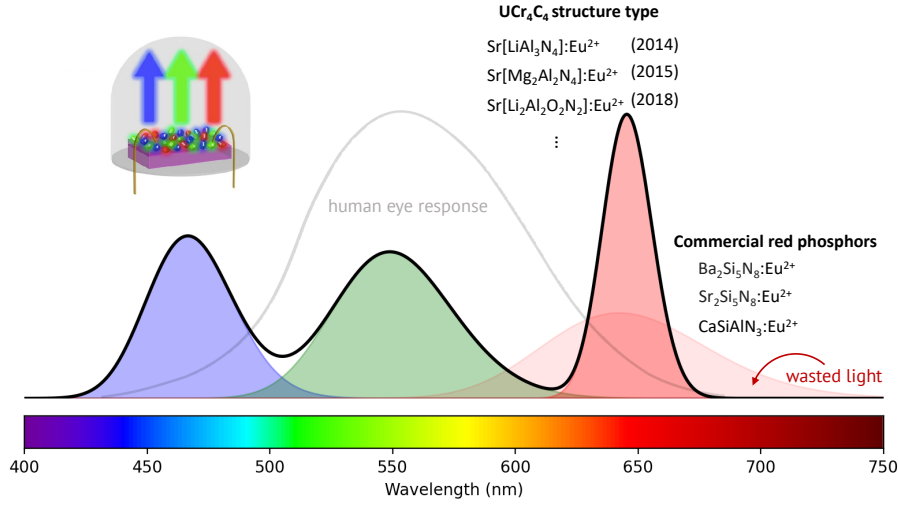


Figure 1.3: Spectral comparison of a narrow bandwidth phosphor and a large bandwidth phosphors with human eye response. The blue and green peaks represent the emission of blue and green phosphors. UCr₄C₄ structure type provides narrower emission than the commercially available red phosphors

red phosphors such as (Sr,Ba)₂S₅N₈:Eu²⁺ [20, 21], or CaSiAlN₃:Eu²⁺ [22, 23] present this issue.

In order to sufficiently cover the red spectral region while minimizing the efficacy loss caused by low eye sensitivity at long wavelengths, red phosphors with very narrow emission bandwidth are needed.

In this quest for new-generation narrow red phosphors [24], materials with UCr₄C₄-type structure [25] doped with Eu²⁺ have recently attracted attention [26, 27]. The first instance of such materials, SrLiAl₃N₄:Eu²⁺ (SLA) phosphor, discovered in 2014 by Schnick and coworkers [28], was quickly followed by other nitride-based phosphors such as CaLiAl₃N₄:Eu²⁺ [29], Sr[Mg₂Al₂N₄]:Eu²⁺ [30] or Sr[Mg₃SiN₄]:Eu²⁺ [31].

Because of the N₈ cuboid environment around the Eu activator, the emission maximum (650 nm in SrLiAl₃N₄:Eu²⁺) is close the edge of the eye sensitivity for red light. Standards in the lighting industry recommends an emission maximum between 610 nm and 620 nm.

To lower the emission wavelength, adding O²⁻ in the cuboid environment like in the oxy-nitride Sr[Li₂Al₂O₂N₂]:Eu²⁺ (SALON) [32] allowed to blue-shift the emission peak to 614 nm, with similar performance than SLA. The crystal structure of such compounds, with similar framework and remarkable one-dimensional cation channels, is presented on figure 1.4.

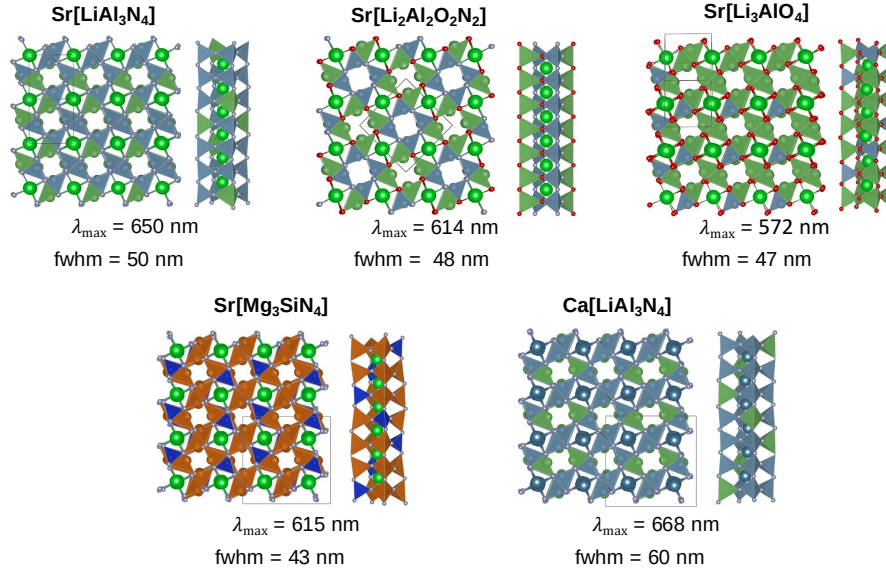


Figure 1.4: Crystal structures of a series of UCr₄C₄-type phosphors, with their corresponding emission peak and full width at half maximum (FWHM) when doped with Eu atom.

Numerous oxide-based phosphors were then developed with general formula $M_4[\text{Li}_3\text{SiO}_4]_4$ where M can be selected from Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and their combination [26, 33–35]. In these compounds, the Eu^{2+} ion replaces a monovalent cation, but the identification of which cation is replaced remains a challenging task [36]. The monovalent substitution also brings the question of charge neutrality. Vacancies on the highly mobile Li sites (resulting in a local variation of the Li/Si distribution in the network) or vacancies on the monovalent cation sites, are hence needed [37, 38]. Most of these alkali lithosilicate phosphors, with O₈ cuboid environment, provide green/cyan/blue emission. With their very narrow emission bandwidth, they may be useful in display applications.

Recently, replacing nitrogen by oxygen and partially replacing Li for Al/Ga in $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ led to two isomorphous compounds : $\text{Sr}[\text{Li}_3\text{AlO}_4]:\text{Eu}^{2+}$ and $\text{Sr}[\text{Li}_3\text{GaO}_4]:\text{Eu}^{2+}$, that provide yellow and green emission, respectively [39].

It is commonly accepted that the narrow-band emission of Eu-doped UCr₄C₄ structure is linked to the highly condensed and rigid host structure. However, the microscopic origin of such narrow emission is not fully understood. One goal of the present work is to elucidate, using

first-principles calculations, the reason for the superior performance (in term of narrow emission bandwidth) of this class of compounds.

1.4 LUMINESCENCE OF LOCALIZED DEFECT CENTER

A rapid estimation of the number of combinations between dopants and matrix host leads to an unreasonable amount of potential luminescent materials, each with unique luminescent properties. Only using Eu^{2+} (main dopant studied in this work, and actually an interesting dopant because of the extreme sensitivity of the Eu_{5d} energy to the matrix host) in all the possible binary, ternary, quaternary,... compounds leads to a variety of properties that can be used in a variety of applications, which is a real material design challenge. In this regards, a theoretical framework allowing to understand and predict these properties is required. Such theoretical approach allows to mitigate the long and most often unsuccessful trial-and-error approach of mixing hosts with dopants.

In a photoluminescence (PL) experiment, light with energy above the bandgap excites electrons from the valence band to the conduction band. Electrons can also be excited from or to defect states. As these excited electrons transition to lower energy levels, they emit light to conserve energy, creating peaks in the PL spectrum. In a photoluminescence excitation (PLE) experiment, the PL intensity is measured as a function of the excitation photon energy, providing an emission or absorption profile for the defect. While these techniques offer high-resolution optical signatures of defects, they cannot alone determine their specific nature or character. This is where comparison with first-principles calculations becomes particularly useful.

1.4.1 *Energy levels*

The link between the macroscopic quantity (the luminescence or excitation spectrum) and the microscopic quantity (the atomic details of the material), often denoted as material-property relationship, is made with the help of quantum mechanics and the subsequent energy levels.

Let us describe qualitatively these energy levels in a static lattice, for the case of lanthanides ions.

Going trough the lanthanide elements in the periodic table, the $4f$ shell becomes filled with n electrons (n going from 1 to 14). For instance,

Ce^{3+} ion has a $[Xe]4f^1$ electron configuration and Eu^{2+} has $[Xe]4f^7$ configuration. This $4f$ shell is considered as an inner shell since it is surrounded by $5p^6$ and $5s^2$ sub-shells of the $[Xe]$ configuration. This means that the crystal field has little influence on the $4f^n$ states and the level spacing between those $4f^n$ states is almost completely influenced by the electron-electron interaction within this $4f$ shell.

Consider now the configuration $[Xe]4f^{n-1}5d^1$, obtained after photon absorption and electron excitation. In this case, the $5d$ orbital extends beyond the $[Xe]$ core and it can strongly interact with the ligand anions. In fact, the crystal field interaction with $5d$ electrons is about 50 times stronger than with $4f$ electrons [40], which also means that the $5d$ -level energies are highly dependent on the type of compound in which lanthanide ion is placed.

4f↔5d transition in Ce^{3+}

The understanding of the $4f$ and $5d$ energy levels of lanthanides ions in various compounds is largely due to the work of Dorenbos, see reference [40] for a review. He analyzed more than 1000 compounds doped with different lanthanides and extracted tendencies and semi-empirical formulas relating $4f$ - $5d$ transition energies to relevant structural parameters for Ce^{3+} [41–43] or Eu^{2+} [44]. A flavor of the "Dorenbos" model is presented below.

For the sake of simplicity, let us take the simplest lanthanide ion to detail the $4f$ - $5d$ transition energy : Ce^{3+} that has only one $4f$ electron (no electron-electron interaction within the $4f$ shell). For visualization, figure 1.5 shows a schematic representation of the relevant Eu^{2+} energy levels in different environments.

4F ENERGY LEVEL As mentioned before, the $4f$ energy level of Ce^{3+} in its $[Xe]4f^1$ electronic configuration does not interact strongly with the crystal field. As a result, only a spin-orbit coupling ($^2F_{5/2} - ^2F_{7/2}$) that is already present in the free ion is observed. In the case of Eu^{2+} , the $4f$ bands split into seven 7F_J states that spread about 0.6 eV in energy [40].

5D ENERGY LEVEL Things are more complicated in the $[Xe]4f^05d^1$ electronic configuration. In that situation, we are in the case of a strong crystal field. For the d orbitals (orbital number $l = 2$), five states are possible ($2l + 1$). In the free ion case, if spin-orbit coupling is ignored,

those five d orbitals are degenerate.

First, consider that the central ion is surrounded by a spherical electrostatic field caused by anion ligands. Due to the preserved spherical symmetry, the five states are still degenerate but the $5d$ energy can be shifted by the *centroid shift* ϵ_c defined as the lowering of the energy of the $5d$ -configuration relative to the value of the free-ion case. This centroid shift is affected by the chemical (covalence) and physical (polarizability) properties of the ligand anions.

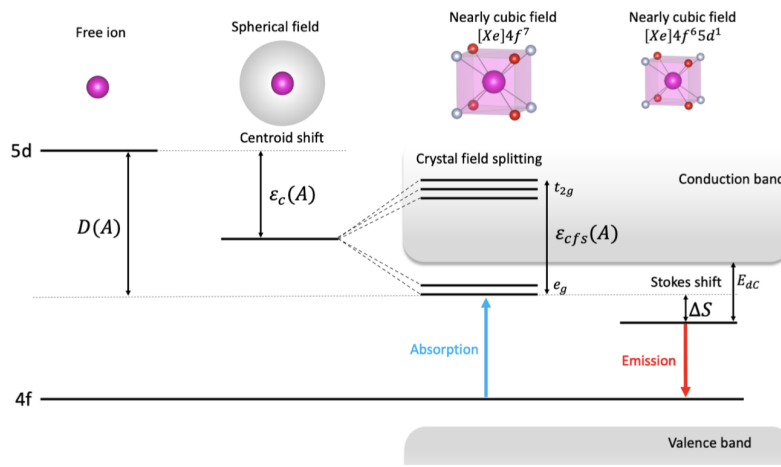


Figure 1.5: Schematic representation of the Dorenbos's model of the $4f$ - $5d$ transition energy of Eu^{2+} ion that has nearly cubic coordination environment composed of oxygen (red) and nitrogen (grey).

Then, we consider that the ligands anions are coordinated in a given polyhedron shape (cubic, tetrahedral,...). The five $5d$ orbitals are not equivalent anymore and they are split in energy. This is known as the *crystal field splitting* that is mainly determined by the size and the shape of the first anion coordination polyhedron around Ce^{3+} . For instance, in a cubic coordination environment, the $5d$ energy levels are split into high-energy t_{2g} states (d_{xy}, d_{xz}, d_{yz}) and low-energy e_g states ($d_{x^2-y^2}, d_{z^2}$) (this is the opposite for octahedral symmetry). Those e_g and t_{2g} orbitals can further split if the anion coordination is not perfectly cubic or if two anion types are involved in the anion coordination polyhedron. This crystal field splitting is characterized by the energy difference between the highest and the lowest $5d$ level noted as ϵ_{cfs} . In total, when accounting for these two effects, a global redshift (decrease in energy) often denoted as $D(A)$ is observed in the $4f$ - $5d$ transition energy (where

A denotes the compound in which the lanthanide ion is included). Of course, this accounts for absorption energy. To determine the 5d-4f emission energy, we have to add the Stokes shift ΔS which is related to the change in the lowest 5d energy due to the atomic relaxation in the excited 5d state (see section on the configuration coordinate model).

Figure 1.5 presents a schematic representation of the model described (often referred to as the Dorenbos's model). The position of the conduction and valence band in the solid was added in this representation. It allows us to define the quantity E_{dC} which is the energy difference between the bottom of the conduction band and the lowest 5d level in the relaxed excited state. This quantity plays an important role in the temperature quenching process through auto-ionization of the 5d electron in the conduction band due to thermal excitation [45].

In appendix B, a qualitative description of the Eu^{2+} energy levels and the corresponding luminescence features is presented. A comparison with the luminescence arising from Eu^{3+} ions is given.

1.4.2 Configuration coordinate model

The configurational coordinate model is often used to explain optical properties, particularly the effect of lattice vibrations, of a localized center. It is in the 1950's with Kun Huang and Avril Rhys that this model was quantitatively used to obtain analytical expressions for the band shapes (luminescence or excitation spectra) [46]. They gave their name to the most important parameter of the model, the so-called Huang-Rhys factor, S .

On the one hand, analysis of experimental results in terms of such a model provides a lot of insight about defects. On the other hand, first-principles calculations comprise a tool that can directly provide such information. Thus, in this regard, the comparison between experiment and theory is a very powerful combination to study defects.

In the textbook description of the configurational coordinate model (CCM), only one vibrational mode is considered (1D), the totally symmetric or breathing mode. This simplification has the important advantage to allow to depict the potential energy surfaces of the ground and excited state only as a function of one normal coordinate, Q , often called the configurational coordinate (see figure 1.6).

If we consider a diatomic molecule, this is the stretching mode and Q is linked to the distance between the two atoms. In the case of a defect cluster, for instance a metal impurity surrounded by eight

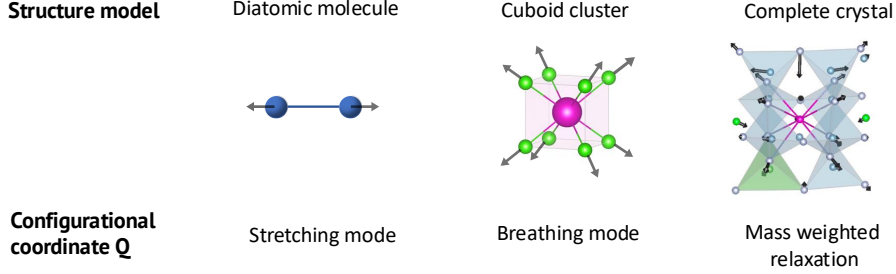


Figure 1.6: Configuration coordinate of different model structures

ligands in a symmetric cuboid, the ‘breathing mode’ is considered and Q is simply the impurity-ligand distance. In the above examples, the underlying assumption for choosing such configuration coordinate Q is the following. When changing electronic state, the associated atomic relaxation is aligned with this chosen coordinate. For the diatomic molecule, this is always true. However, already in the case of the cuboid cluster, it might be that the change in electronic state leads to a distortion of the cuboid. To take care of this, and in general to deal with any kind of atomic relaxation, we choose Q to be a configuration coordinate that follows this relaxation, or in other words, that linearly interpolates between the atomic positions of the excited state and the atomic positions of the ground state. Indeed, this requires to know the relaxation. The change in configuration coordinate between the two electronic states ΔQ , also called normal coordinate change, is computed as :

$$(\Delta Q)^2 = \sum_{\kappa, \alpha} M_{\kappa} (\Delta R_{\kappa, \alpha})^2, \quad (1.1)$$

where $\Delta R_{\kappa, \alpha} = R_{\kappa, \alpha}^{ex} - R_{\kappa, \alpha}^g$ is the change in position of atom κ , with mass M_{κ} , along direction α between electronic excited and ground state. One can also quantify the total atomic displacements (ΔR) as :

$$(\Delta R)^2 = \sum_{\kappa, \alpha} (\Delta R_{\kappa, \alpha})^2. \quad (1.2)$$

The extent of atomic relaxation is associated with how localized a defect’s wavefunction is, or more precisely, with the difference in localization between the initial and final wavefunctions. When a wavefunction is delocalized, the electron density at the defect is low, exerting minimal influence on the atomic positions—this is typical of shallow defect states. In contrast, if the wavefunction is localized (either on the defect

itself or on a few neighboring atoms), it significantly impacts the local atomic arrangement when the defect electronic state changes. In this work, we will concentrate on this latter category of deep, localized defect states.

Stokes shift

Following the Condon approximation [47], the electronic transition associated to photon absorption/emission occurs vertically, leaving the atomic coordinates unchanged, as illustrated on figure 1.7 left. Suppose that we start in the electronic ground state and vibrational ground state. After photon absorption and electron excitation, and due to a non-zero normal coordinate change ΔQ , the vibrational state created is not the vibrational ground state. The electronic transition is hence accompanied by an atomic relaxation towards the new vibrational ground state of the electronic excited state. In this non-radiative process, phonons (quanta of vibrations) are created. The electronic excited state will then decay radiatively to the electronic ground state, in a non-equilibrium atomic geometry. As for absorption, emission is followed by atomic relaxation and phonon creation.

The change in energy between emission and absorption energy is called the Stokes shift ΔS :

$$\Delta S = E_{abs} - E_{em},$$

and is the total energy transferred in the lattice after a sequence of excitation-relaxation-decay-relaxation. We note that the underlying assumption behind this fixed sequence is that the difference in timescale at which these phenomena occurs is large. In particular, $\tau_{relaxation} \ll \tau_{decay}$.

Lineshape

From this simple displaced harmonic oscillators problem, a semi-classical picture can already bring useful information about the emission shape. We consider that we are in the first quantum vibrational state in the electronic excited state (as depicted in red on figure 1.7, left), with a Gaussian vibrational wavefunction χ_0 . The probability density $|\chi_0|^2$ associated to this state follows also a Gaussian distribution. In the case of a cuboid cluster for instance, the most probable atomic configuration is the relaxed geometry and increasing the ion-ligands distance

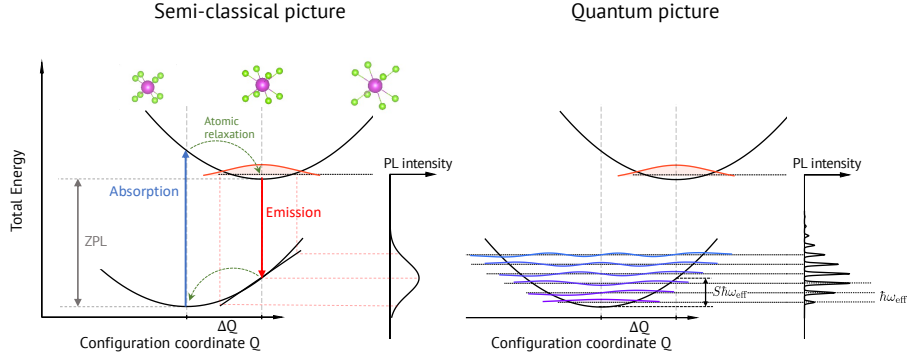


Figure 1.7: Semi-classical (left) versus quantum (right) picture of the displaced harmonic oscillators model to understand luminescence lineshape. Only the first vibrational state is shown in the electronic excited state for the full quantum picture, as it is the only one contributing at 0K. ZPL refers to the zero-phonon line.

reduces the likelihood of finding this configuration with a Gaussian decay. While intuitive, this is a quantum effect. In a classical harmonic oscillator, the relaxed geometry is the least probable configuration (where the oscillator momentum is at its maximum). Considering that the transition occurs vertically, one can map this probability density to a Gaussian-shaped spectrum, assuming linearity around ΔQ , as shown in figure 1.7. This spectrum is centered around the emission energy, and its full width at half maximum can be computed analytically, see equation 1.7 below.

Let us now consider a quantum picture where the two potential energy surfaces are quantum harmonic oscillators with effective frequency ω_{eff} that are displaced with each other by ΔQ . We consider here an effective frequency to reflect the fact that the atomic relaxation accompanied by the electronic transition can be thought as an effective vibrational mode that couples with this transition (see additional details in the next chapter). These oscillators lead to discrete vibrational energy levels, labeled by n , with energy

$$E_n = (n + 1/2)\hbar\omega_{\text{eff}} \quad (1.3)$$

Harmonic oscillators eigenfunctions are Hermite polynomials χ_n . In addition, the transition probability follows the square of the overlap between the initial and final harmonic oscillators eigenfunctions (the Franck-Condon factors), which writes for emission $|\langle\chi_{g,n}|\chi_{e,m}\rangle|^2$. $\chi_{g,n}$

$(\chi_{m,e})$ is the vibrational wavefunction in state n (m) in the electronic ground (excited) state.

For the special case of similar oscillators frequencies and at 0K, where only the state $m=0$ contributes, a concise expression exists to calculate the transition probabilities [48]:

$$|\langle \chi_{g,n} | \chi_{e,0} \rangle|^2 = e^{-S} \frac{S^n}{n!}, \quad (1.4)$$

with S the Huang-Rhys factor, a dimensionless constant giving the mean number of effective phonons of frequency ω_{eff} involved in the electronic transition :

$$S = \frac{\frac{1}{2}\omega_{\text{eff}}^2 \Delta Q^2}{\hbar\omega_{\text{eff}}} = \frac{\omega_{\text{eff}} \Delta Q^2}{2\hbar}. \quad (1.5)$$

As shown on figure 1.7, right, $S\hbar\omega_{\text{eff}}$ is the total energy lost in the lattice during atomic relaxation, and is often referred as the Franck-Condon energy. The emission band shape $A(\hbar\omega)$, function of the photon energy $\hbar\omega$ is hence given by a series of lines, starting at the so-called zero-phonon line (ZPL), with intensities following a Poisson distribution. We write

$$A(\hbar\omega) = \sum_n e^{-S} \frac{S^n}{n!} \delta(E_{\text{ZPL}} - n\hbar\omega_{\text{eff}} - \hbar\omega). \quad (1.6)$$

Dirac delta are used for energy conservation, and are typically replaced by Gaussian or Lorentzian functions with a choosen width in simulations. In the next chapter, it will be shown how more realistic lineshapes can be obtained by alleviating the single phonon mode hypothesis. In the semi-classical formulation, and following the linear mapping shown above, one can find formulas for the full width a half maximum of the emission shape [49] :

$$W(0) = \sqrt{8\ln 2} \sqrt{S\hbar\omega_{\text{eff}}}. \quad (1.7)$$

Averaging the Bose-Einstein occupations of the initial vibrational states allows one to compute the temperature dependent FWHM :

$$W(T) = W(0) \sqrt{\coth\left(\frac{\hbar\omega_{\text{eff}}}{2k_B T}\right)}. \quad (1.8)$$

The semi-classical approximation is actually valid in the case of strong coupling (large Huang-Rhys factor), where the Poisson distribution

approaches a Gaussian distribution, and where the phonon peaks are faded out in profit of a featureless smooth spectrum. In such case, fitting equation 1.8 on experimental measurements allows one to estimate both the effective phonon frequency ω_{eff} and the Huang-Rhys factor S . Another way to estimate S is to estimate the PL weight of the zero-phonon line w_{ZPL} , and to use the relation $w_{\text{ZPL}} = e^{-S}$.

To illustrate the importance of the Huang-Rhys factor S , figure 1.8 presents the emission band shape for different S and different temperatures. The quantum picture, with clear phonon peaks, is compared to the semi-classical formulation. At very low Huang-Rhys factor (small coupling), most of the intensity comes in the ZPL line, with small contribution of the phonon side band. At $S=1.5$ (intermediate coupling), the asymmetry of the Poisson distribution is still visible. At $S=7$ (large coupling), the global shape is very well approximated by the Gaussian semi-classical model, and the ZPL intensity is close to zero. An increase in temperature gives rise to transitions starting from higher initial vibrational states, provoking an increase in the intensity of the so-called anti-Stokes lines. The band shape spreads in energy and approaches a Gaussian shape.

The magnitude of S is the largest when the charge distribution of the defect electron changes a lot in the transition. It also depends on the scale of the wavefunction. For a very diffuse function, the elastic energy is sufficient to prevent large displacements, giving small S . Another case where S is small is for transitions within the 3d or 4f shells of transition metals ions. This is the case in the very sharp Mn^{4+} or Eu^{3+} lineshapes for instance.

In the field of luminescence, the important measured macroscopic quantity is often a featureless nearly Gaussian shaped emission/excitation spectrum. Identifying the localized center responsible for the luminescence is a difficult and critical process. It is often based on assumptions, confirmed by experiments or simulations. Sometimes, the responsible center makes a obvious consensus (" Eu^{2+} has a similar radii than Sr^{2+} and similar charge, it should substitute it"). Sometimes, the center responsible for luminescence is less obvious. Two centers might provide very similar spectra, leading to an extremely difficult distinction between the two.

When a spectrum, especially at low temperature, presents fine features such as phonon peaks (also called vibronic peaks), a careful examination of these peaks often allows to gain important insights into the luminescence microscopic atomic origin. Being able to simulate the

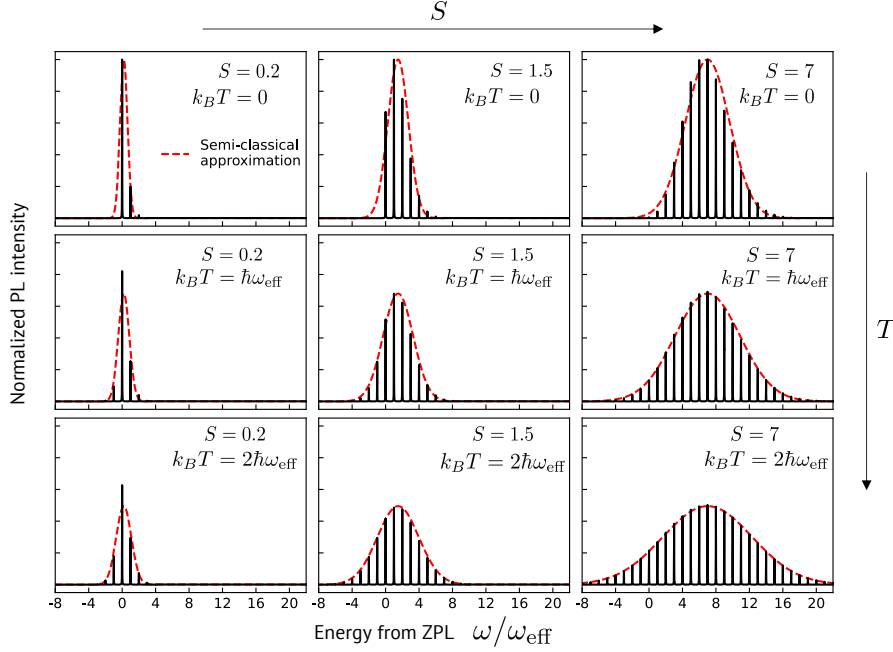


Figure 1.8: Emission band shape for different Huang-Rhys factor and different temperatures. The quantum formulation (black), with apparent vibronic peaks, is compared with a semi-classical formulation (red-dashed).

vibronic peaks that would results from a given luminescent center is a precious tool that allows a straightforward comparison with experimental measurements. If simulation and experiment agrees at the level of the PL spectrum and its vibronic peaks, the likelihood that the simulated center is the correct "real life" center increases substantially. This calls for (1) a theoretical framework allowing to simulate in a computationally tractable way real PL spectra and (2) when possible, systematic low-temperature PL measurements allowing to resolve phonon peaks.

As a final remark, we clarify the terminology of "narrow emission" used in this work. Here, the spectral width of the emission is determined by the coupling strength between the electronic transition and phonons, typically ranging from approximately 0.1 to 1 eV. "Narrow emission" refers to spectra with FWHM on the lower end of this range. However, it is important to place this definition in context. In lanthanide systems involving f-f transitions, such as those of Eu^{3+} , the intra-configurational nature of these transitions, along with the shielding of 4f electrons by outer electron shells, leads to significantly sharper spectral features. These emissions are much narrower than those in-

fluenced by electron-phonon interactions, highlighting the distinction between different types of "narrow emission" in solid-state systems.

LUMINESCENCE LINESHAPE OF DEFECT CENTER

In this chapter, we show the steps leading to a formulation of the luminescence lineshape originating from a defect center, in a more rigorous way, and by considering all the vibrational modes of the system. Starting from the Born-Oppenheimer approximation, it is shown how linear electron-phonon interaction brings a phonon side band in the PL lineshape. The generating function approach, which allows to compute the multi-dimensional lineshape efficiently in the time domain, is presented. A connection with the effective mode model (chapter 1) is made. Relevant theoretical references includes classical books [49–55], foundational papers [46–48, 56, 57], or more recent papers written in the context of defect centers for quantum technologies (NV-center like) [58, 59].

2.1 LINEAR ELECTRON-PHONON INTERACTION

We place ourselves within the Born-Oppenheimer approximation, allowing to treat separately the electron dynamic and the nuclei dynamic. The electronic Schrödinger equation is written as :

$$\left(- \sum_{el} \frac{1}{2m_{el}} \nabla_{el}^2 + V(\mathbf{r}, \mathbf{R}) \right) \psi_i(\mathbf{r}) = \epsilon_i(\mathbf{R}) \psi_i(\mathbf{r}), \quad (2.1)$$

where $V(\mathbf{r}, \mathbf{R})$ is the potential felt by the electrons of mass m_{el} and located at a set of positions $\mathbf{r}$, $\psi_i(\mathbf{r})$ and $\epsilon_i(\mathbf{R})$ are the many-body electronic eigenfunctions and eigenenergies with fixed nuclei of masses M_κ at the set of positions $\mathbf{R}$. As the positions $\mathbf{R}$ change over time, both $\psi_i(\mathbf{r})$ and $\epsilon_i(\mathbf{R})$ follow this change adiabatically, while the system stays in electronic state i . The atomic problem is written as :

$$\left(- \sum_{\kappa} \frac{1}{2M_{\kappa}} \nabla_{\kappa}^2 + \epsilon_i(\mathbf{R}) \right) \chi_{i,n}(\mathbf{R}) = E_{i,n} \chi_{i,n}(\mathbf{R}), \quad (2.2)$$

where the eigenenergies of the electronic problem $\epsilon_i(\mathbf{R})$ (the so-called "Born-Oppenheimer surfaces") play the role of the potential in which the nuclei move. The $\chi_{i,n}(\mathbf{R})$ are the nuclei (or vibrational) eigenfunctions and depend on the electronic state i . The total wavefunction of the system is the product of the electronic and vibrational eigenfunctions : $\Psi_{i,n}(\mathbf{r}, \mathbf{R}) = \psi_i(\mathbf{r})\chi_{i,n}(\mathbf{R})$

Expanding the Born-oppenheimer surfaces up to second-order with respect to the atomic displacements around their equilibrium positions (harmonic approximation) allows to compute the allowed vibrational modes of the system, in a classical sense. $3N$ (N being the number of atoms in the cell) normal modes of vibrations, labeled with ν letter are obtained by solving a generalized eigenvalue equation :

$$M_{\kappa}\omega_{\nu}^2 e_{\nu,\kappa\alpha} = \sum_{\kappa'\alpha'} C_{\kappa\alpha,\kappa'\alpha'} e_{\nu,\kappa'\alpha'}, \quad (2.3)$$

with $C_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial^2 E}{\partial R_{\kappa'\alpha'} \partial R_{\kappa\alpha}}$ the interatomic force constant (IFCs) matrix. The total energy E can be the one of the electronic ground state, as computed with DFT for instance. These modes are independent from each other, and characterized by vibrational frequencies ω_{ν} (eigenfrequencies) and a pattern of atomic displacements, or normal modes of vibration $e_{\nu,\kappa\alpha}$ (eigenvectors). Introducing the corresponding normal coordinate Q_{ν} , one can rewrite the potential energy surfaces and make the appearance of harmonic oscillators clear :

$$\epsilon_i = \epsilon_i^{eq} + \frac{1}{2} \sum_{\nu} \omega_{\nu}^2 Q_{\nu}^2. \quad (2.4)$$

Solving equation 2.2 with such a potential allows to retrieve a set of $3N$ independent quantum harmonic oscillators, with solutions giving discrete vibrational energy levels

$$E_{\nu}^{vib} = (n_{\nu} + \frac{1}{2})\hbar\omega_{\nu}, \quad (2.5)$$

and individual orthogonal vibrational eigenfunctions $\chi_{n_{\nu}}(Q_{\nu})$ that takes a well known mathematical form (Hermite polynomials), and whose product form the total vibrational eigenfunction :

$$\chi_{\mathbf{n}}(Q) = \prod_{\nu} \chi_{n_{\nu}}(Q_{\nu}). \quad (2.6)$$

Bold symbol $\mathbf{n}$ is a compact notation that refers to the set of vibrational states $[n_1, n_2, \dots, n_{3N}]$. Coming back now to the electronic problem, by

expanding in first order the potential with respect to the phonon normal coordinates,

$$V(Q_\nu) = V(0) + \left. \frac{\partial V}{\partial Q_\nu} \right|_{Q_\nu=0} Q_\nu, \quad (2.7)$$

we add a linear electron-phonon term to equation 2.4 [60]:

$$\epsilon_i = \epsilon_i^{eq} + \frac{1}{2} \sum_\nu \omega_\nu^2 Q_\nu^2 + \frac{1}{\sqrt{3N}} \sum_\nu \langle \psi_i | \frac{\partial V}{\partial Q_\nu} | \psi_i \rangle Q_\nu. \quad (2.8)$$

The linear correction induced by the electron-phonon interaction depends on the electronic state i . This means that the Born-Oppenheimer surfaces will all be shifted with respect to each other, with a shift that depends both on the phonon mode ν and the electronic state i . Vibrational eigenfunctions corresponding to different electronic states are no longer orthogonal, $\langle \chi_{j,m} | \chi_{i,n} \rangle \neq 0$. From a point of view of the lattice, the correction reflects the fact that a change in electronic state induces a change in the equilibrium positions of the atoms. When changing the electronic state by absorbing/emitting a photon, transition between different vibrational levels hence comes with non-zero intensity, giving rise to a phonon-side band in the luminescence lineshape.

In the above development, note that we truncated our expansion to the first order with respect to the phonon normal coordinates, leading to the same Born-Oppenheimer curvatures between electronic states. A second-order expansion would lead to eigenfrequencies that depend on the electronic state $\omega_{\nu,i}$.

2.2 FERMI'S GOLDEN RULE

We aim at studying the dipole allowed transition between two states (the ground state labelled g and the excited state labelled e) brought by a defect atom within a host material. Following Fermi's golden rule [61, 62], the absolute luminescence intensity $I(\hbar\omega)$ (number of photons emitted per unit time per unit energy) is expressed as a function of the photon energy $\hbar\omega$ as

$$I(\hbar\omega) = \frac{n_D \omega^3}{3\pi \hbar \epsilon_0 c^3} |\mu_{ge}|^2 \delta(E_g - E_e - \hbar\omega), \quad (2.9)$$

where n_D is the material refractive index, $\mu_{ge} = \langle \Psi_g | \mu | \Psi_e \rangle$ is the total dipole matrix element with μ the dipole operator. E_e and E_g are the total energies and contain the electronic and vibrational energies.

It is typically assumed that the electronic part of the dipole matrix element between the excited and ground states depends weakly on the nuclear coordinates (Franck-Condon approximation), this allows one to split the matrix elements into a purely electronic part and a purely vibrational part :

$$|\mu_{ge}|^2 = |\mu_{ge}^{el}|^2 |\langle \chi_{g,n} | \chi_{e,m} \rangle|^2. \quad (2.10)$$

The inverse of the electronic part is a direct measure of the radiative lifetime, while the vibrational part controls the band shape of the emitted spectrum. We define the normalized luminescence intensity as

$$L(\hbar\omega) = C\omega^3 A(\hbar\omega), \quad (2.11)$$

with C a normalization constant. In the case of the absolute intensity $I(\hbar\omega) = C\omega^3 A(\hbar\omega)$, $C = \frac{n_D}{3\pi\hbar\epsilon_0 c^3} |\mu_{ge}^{el}|^2$. The emission lineshape function $A(\hbar\omega)$, which dictates the shape of the spectrum, must account for all available transitions. That is, for a given mode ν , from an initial vibrational state m_ν to any final vibrational state n_ν . Mode mixing should also be included : a peak in the luminescent spectrum could originate from the emission of two phonons of a given mode, and one phonon of another mode. Temperature might also be included by adding a Bose-Einstein thermal occupation factor p_{m_ν} for initial vibrational states which gives

$$A(\hbar\omega) = \sum_{n,m} p_{m_\nu}(T) |\langle \chi_{g,n} | \chi_{e,m} \rangle|^2 \delta(E_{ZPL} - E_{g,n} + E_{e,m} - \hbar\omega). \quad (2.12)$$

Since the total vibrational states $\chi_{e,m}$ and $\chi_{g,n}$ are the product of $3N$ independent harmonic oscillator eigenfunctions as written in equation 2.6, we have :

$$|\langle \chi_{g,n} | \chi_{e,m} \rangle|^2 = \prod_{\nu} |\langle \chi_{g,n_\nu} | \chi_{e,m_\nu} \rangle|^2. \quad (2.13)$$

The E_{ZPL} is the so-called zero-phonon line energy (purely electronic energy difference assuming that the ground and excited state phonon frequencies are identical), $E_{g,n} = \sum_{\nu} n_{\nu} \hbar\omega_{g,\nu}$ is the vibrational energy of state $\chi_{g,n}$ (and likewise for $E_{e,m}$). Notice that $\sum_{n,m}$ compactifies two $3N$ infinite sums : $\sum_{n,m} = \sum_n \sum_m$ with $\sum_n = \sum_{n_1} \sum_{n_2} \dots \sum_{n_{3N}}$.

The vibrational modes of the excited and ground states can be in principle different, both in terms of frequency and normal mode (Dusch-

insky effect [63]), making equation 2.12 computationally expensive because of the highly multidimensional integrals to be evaluated (Franck-Condon overlaps). Throughout this work, we will assume that the vibrational modes in the excited electronic state are identical to those in the ground state (equal mode approximation).

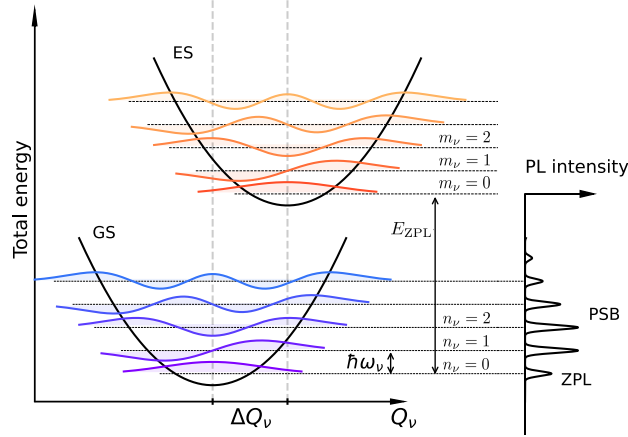


Figure 2.1: Schematic representation of the origin of photoluminescence (PL) spectra. On the left, ground state (GS) and excited state (ES) energy curves are projected along phonon normal coordinate Q_v and are approximated by harmonic functions with the same frequency ω_v . Vibrational energy levels and corresponding eigenfunctions are shown as horizontal lines and colored areas. GS and ES are displaced by ΔQ_v , the mass-weighted displacement between the minimum of the GS and the ES curves. On the right, the PL spectrum is formed. The zero-phonon line (ZPL) comes from the transition between the first vibrational level of the ES to the first vibrational level of the GS. Other transitions give the phonon sideband (PSB). The intensity of each peak is computed with the overlap between corresponding eigenfunctions

A careful inspection of equation 2.12 reveals that, due to the multiplicative properties of the independent vibrational overlaps, the total lineshape $A(\hbar\omega)$ is just a 3N convolution of the lineshapes which could be obtained by coupling to each phonon mode separately.

$$A(\hbar\omega) = A_1(\hbar\omega) \otimes A_2(\hbar\omega) \otimes \dots \otimes A_{3N}(\hbar\omega) \quad (2.14)$$

where $A_v(\hbar\omega)$ can be obtained from equation 1.6 if we considered $T=0K$. We rewrite equation 1.6

$$A_v(\hbar\omega) = \sum_{n_v} e^{-S_v} \frac{S_v^{n_v}}{n_v!} \delta(E_{ZPL} - n_v \hbar\omega_v - \hbar\omega), \quad (2.15)$$

to make clear that we now need the individual phonon frequencies $\hbar\omega_\nu$ and corresponding individual (or partial) Huang-Rhys factor S_ν . The individual lineshape obtained is depicted on figure 2.1.

These partial Huang-Rhys factors tells by how much a given phonon mode couples to the electronic transition. They are obtained thanks to the equation

$$S_\nu = \frac{\omega_\nu \Delta Q_\nu^2}{2\hbar}, \quad (2.16)$$

where the ΔQ_ν are the mass-weighted atomic displacement projected along the phonon mode ν

$$\Delta Q_\nu = \sum_{\kappa\alpha} \sqrt{M_\kappa} \Delta R_{\kappa\alpha} e_{\nu,\kappa\alpha}. \quad (2.17)$$

These ΔQ_ν can be seen in the following way : after emission/absorption of a photon, the electronic state changes. This local change in electronic density leads to a (local) atomic relaxation. Since atomic displacements can always be decomposed into a superposition of phonon eigenvectors, we compute the contribution of a given phonon mode to this relaxation by projecting (dot product) the atomic displacements onto the corresponding phonon eigenvector.

The Huang-Rhys spectral function, that encapsulates all the partial Huang-Rhys factors S_ν is defined as :

$$S(\hbar\omega) = \sum_\nu S_\nu \delta(\hbar\omega - \hbar\omega_\nu). \quad (2.18)$$

Figure 2.2 illustrates, with a toy model, the effect of different Huang-Rhys spectral function on the final lineshape function, with a coupling with four phonons modes with different frequencies ω_ν and Huang-Rhys factors S_ν . A arbitrary broadening was added for visualization. The three different regimes (weak, intermediate and strong coupling) are presented, similarly to figure 1.8. From a distance, the global shape of the spectra present similarities to the single effective phonon mode model presented in the previous chapter. This is especially the case in the strong coupling regime, where an effective phonon mode model provides already an accurate description of the luminescence lineshape. However, the consideration of multiple phonon modes allows to capture much richer vibronic progression (as sometimes seen in experiments) in the case of weak and intermediate coupling (as a rule of thumb, when $S < 5$).

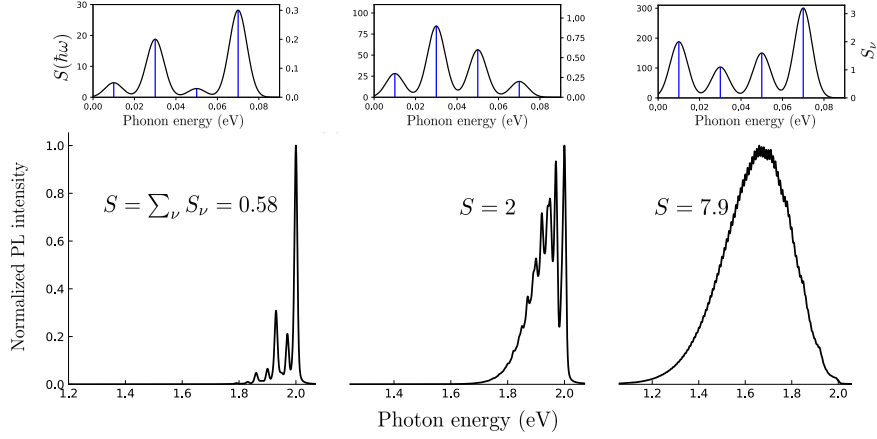


Figure 2.2: Lineshape functions (bottom) associated to different Huang-Rhys spectral functions (top). Three different regimes (weak, intermediate and strong coupling) are presented. The ZPL energy is fixed at 2 eV and $T=0K$.

2.3 GENERATING FUNCTION APPROACH

When dealing with $3N$ phonons with N being large, a direct evaluation of equation 2.12 is impractical. Instead, the mathematically equivalent generating function approach, developed by Lax [47] and Kubo [57] in the fifties, and latter by Dexter [64], is used. The lineshape function $A(\hbar\omega, T)$ is evaluated as the Fourier transform of the generating function $G(t)$

$$A(\hbar\omega, T) = \int_{-\infty}^{+\infty} G(t, T) e^{i\omega t - \frac{\gamma}{\hbar}|t| - i\frac{E_{ZPL}}{\hbar}t} dt, \quad (2.19)$$

with

$$G(t, T=0) = e^{S(t) - S(0)}, \quad (2.20)$$

where $S(t) = \sum_{\nu} S_{\nu} e^{i\omega_{\nu} t}$ is the Fourier transform of the Huang-Rhys spectral function (we have used the Fourier properties of the δ function). γ is a constant homogeneous Lorentzian broadening associated to each vibronic transition. This broadening is typically assumed constant and fitted to the experimental width of individual lines.

While working in the time domain, the effect of temperature (transitions involving initial vibrational states $m_{\nu} \neq 0$, weighted by Bose-Einstein occupation) can be included straightforwardly by rewriting the generating function

$$G(t, T) = e^{S(t) - S(0) + C(t, T) + C(-t, T) - 2C(0, T)}, \quad (2.21)$$

with $C(t, T) = \sum_{\nu} \bar{m}_{\nu}(T) S_{\nu} e^{i\omega_{\nu} t}$ the Fourier transform of the temperature weighted Huang-Rhys spectral function and $\bar{m}_{\nu}(T)$ the average occupation number of ν -th phonon mode:

$$\bar{m}_{\nu}(T) = \frac{1}{e^{\frac{\hbar\omega_{\nu}}{k_B T}} - 1}. \quad (2.22)$$

2.4 CONNECTION WITH THE EFFECTIVE PHONON MODE MODEL

One can connect the multi-phonon modes methodology to the simpler effective phonon mode model presented in chapter 1. The total normal coordinate change ΔQ , due to the orthonormality of the phonon eigenvectors is linked through the partial ΔQ_{ν} through :

$$(\Delta Q)^2 = \sum_{\nu} (\Delta Q_{\nu})^2, \quad (2.23)$$

and allows one to define the weight by which a mode contributes to the total atomic relaxation :

$$p_{\nu} = (\Delta Q_{\nu} / \Delta Q)^2. \quad (2.24)$$

It is then possible to define an effective frequency as

$$\omega_{\text{eff}}^2 = \sum_{\nu} p_{\nu} \omega_{\nu}^2, \quad (2.25)$$

and the total Huang-Rhys factor as :

$$S = \sum_{\nu} S_{\nu}. \quad (2.26)$$

2.5 SUMMARY OF THE APPROXIMATIONS AND PHYSICAL INTERPRETATION

Let us recap the approximations that allowed us to obtain a final computationally tractable equation of the lineshape. Under the Born-Oppenheimer approximation, the atomic displacements are considered as a superposition of $3N$ quantum harmonic oscillators. Within a linear electron-phonon regime, the energy levels brought by the defect possesses a linear dependence in the phonon normal coordinates, that goes as $\langle \psi_i | \frac{\partial V}{\partial Q_{\nu}} | \psi_i \rangle Q_{\nu}$. The electronic ground and excited states of the defect will hence experience different linear correction, leading to an

offset ΔQ_ν , reducing the problem to two displaced quantum harmonic oscillators. The correction being linear, one assumes that the phonon frequencies are the same in the ground and excited electronic state.

Regarding the luminescence lineshape, the emitting center is considered as a two-level system coming from an isolated point defect immersed in a pristine matrix (the bulk). The Franck-Condon approximation is made, assuming that the electronic dipole matrix does not depend on nuclear coordinates, allowing to write the total transition probability as the product of a purely electronic dipole matrix element and of the square of the overlap between non-orthogonal vibrational wavefunctions of the initial and final state. Duschinski effects (mixing of the ΔQ_ν) are neglected, reducing the Franck-Condon overlaps to a product of $3N$ one-dimensional Franck-Condon overlaps.

2.6 WHAT SHOULD BE COMPUTED

From the above approximations, we have seen that the PL lineshape of a point defect embedded in a solid is uniquely defined by the Huang-Rhys spectral function $S(\hbar\omega)$ and the zero-phonon line. In order to compute it from first-principles, we need to obtain :

- The zero-phonon line energy, which is the total energy difference between the electronic excited and ground states of the system.
- The atomic relaxation associated to the change in electronic state, obtained as the difference between the relaxed atomic positions of the excited state and relaxed atomic positions of the ground state.
- The vibrational modes of the system. Note that in the case of the effective phonon model, this is not required since the effective mode is obtained from the atomic relaxation.

The next chapter shows how to obtain these quantities using supercells in the framework of density functional theory with periodic boundary conditions.

MODELING DEFECT LUMINESCENCE WITH DENSITY FUNCTIONAL THEORY

This chapter presents how the theory shown in chapter 2 is implemented in practice, in the framework of density functional theory (DFT) with periodic boundary conditions. Only the methods and equations relevant to the computation of the PL lineshape of a defect center are presented in this chapter. More comprehensive reviews covering many other aspects and subtleties of the computation of points defects in solids from first-principles can be found in references [65–68].

3.1 THE SUPERCELL METHOD

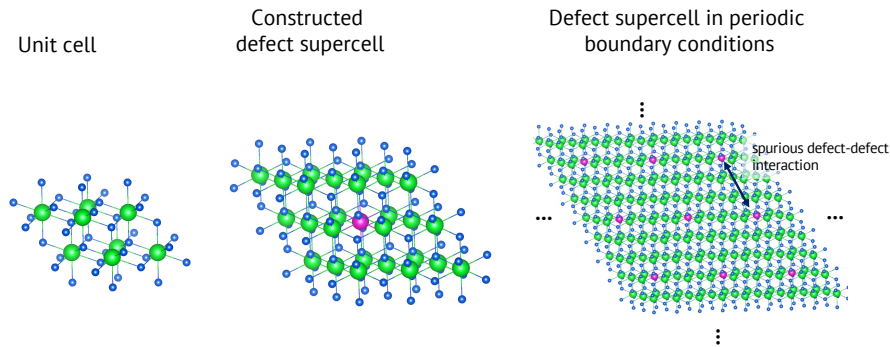


Figure 3.1: The construction a defect supercell model structure of $\text{SrCl}_2:\text{Eu}^{2+}$ from a SrCl_2 unit cell structure. The right panel shows the origin of spurious defect-defect interaction in computations involving periodic boundary conditions.

In first-principles methods like Density Functional Theory (DFT) with periodic boundary conditions, the supercell approach is the pre-

dominant technique [65] for dealing with defects. A large cell, called “supercell”, that contains many more atoms than the primitive cell of the host material is built. Vacancies or substitutions are introduced by removing or replacing atoms. This method retains periodic boundary conditions but uses an enlarged repeating unit. This approach capitalizes on the efficiency and robustness of established computational codes for perfect periodic solids, ensuring a precise description of the pristine host material. However, the caveat is that the supercell method inherently replaces an isolated defect with a periodic array of defects, as illustrated in figure 3.1. This results in unrealistically high defect concentrations, leading to artificial interactions among defect replicas that must be rigorously controlled.

These spurious interactions, which include quantum-mechanical (wave function overlap), elastic, magnetic, and electrostatic effects, do not fundamentally undermine the supercell method as they diminish with increasing supercell size. However, achieving full convergence often requires supercell sizes so large as to be computationally unfeasible. Therefore, it is imperative to accurately estimate the magnitude and decay of these effects, employ strategies to mitigate their impact on computational results, and possibly apply post-calculation corrections. As an example of such corrections, the treatment of charged defect requires to correct the long-range Coulomb defect-defect interaction, for which a number of schemes have been developed [69–72].

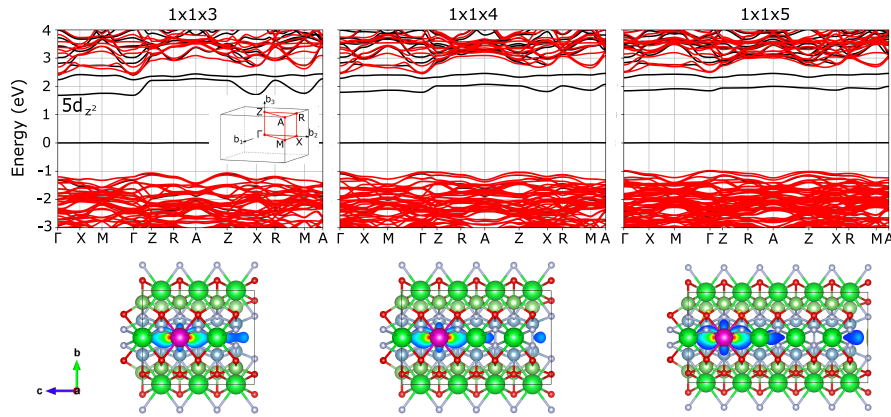


Figure 3.2: Electronic band structure of $\text{Sr}[\text{Al}_2\text{Li}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ for different supercell sizes. The occupied $5d_z^2$ band presents a decreasing dispersive behaviour along Γ -Z with an increase of the supercell size along c -axis. A section representation of the corresponding Kohn-Sham orbitals is shown at the bottom.

Let us demonstrate the impact of artificial defect-defect interactions with two examples.

First, the overlap of defect wave functions between neighboring supercells may cause the single-particle state of an isolated defect to transform into a dispersive defect band. This phenomenon is illustrated in figure 3.2, where the dispersive nature of the $5d_{z^2}$ state along Γ -Z becomes significant when the supercell size along the c axis is too small. By increasing the supercell size, the dispersion decreases. It is possible to show that a deep defect band disperses around the level of the isolated defect, as seen in figure 3.2. For a localized state within the band gap, the defect wave function decays exponentially as it moves away from the defect center [65]. Consequently, the overlap matrix elements between wavefunction replicas decrease exponentially with an increase in supercell size.

Second, and perhaps more critically when calculating a luminescence lineshape, the interaction between defect replicas can lead to cancellations in the determination of atomic displacements induced by the change in electronic state, as shown in figure 3.3. This effect can be particularly problematic when the displacements extend far from the defect, exhibiting long-range behavior [73]. In such cases, achieving strict convergence requires a significantly larger supercell size. The embedding section of this chapter will discuss methods to mitigate this effect.

3.2 Δ SCF CONSTRAINED OCCUPATION

DFT is formally a theory of the ground state, and one has to go beyond DFT to treat excited states. For neutral excitations (like in the case of $4f$ - $5d$ transition), the Bethe-Salpeter of many-body perturbation theory [74] is considered the state of the art to capture the electron-hole interaction. Unfortunately, the computational cost and memory needed for such approach are prohibitive for supercell sizes required to obtain meaningful results. Instead, the constrained-occupation Δ SCF [75, 76] method is used to simulate the excited state, and allows to obtain the ZPL energy E_{ZPL} , the pattern of atomic displacements $\Delta R_{\kappa\alpha}$ and forces $\Delta F_{\kappa\alpha}$. It refers to the use of DFT with non-Aufbau electronic occupations (the energy levels are not filled from the lowest to highest energy) to mimick the electron-hole interaction. Transition energies are computed by taking the differences between total DFT energies with different occupations (Δ SCF). It started in atomic physics or core-level spectro-

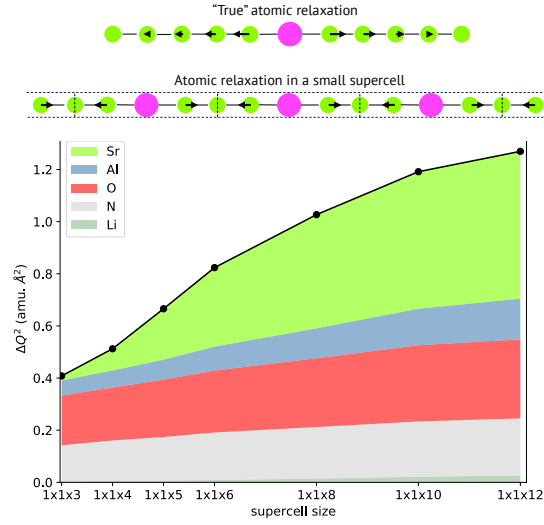


Figure 3.3: An illustration of the slow convergence of the total normal coordinate change (mass weighted atomic relaxation) with the supercell size increase, from [73]. Since the *true* relaxation presents a long-range behavior, cancellation errors remain large in small supercells.

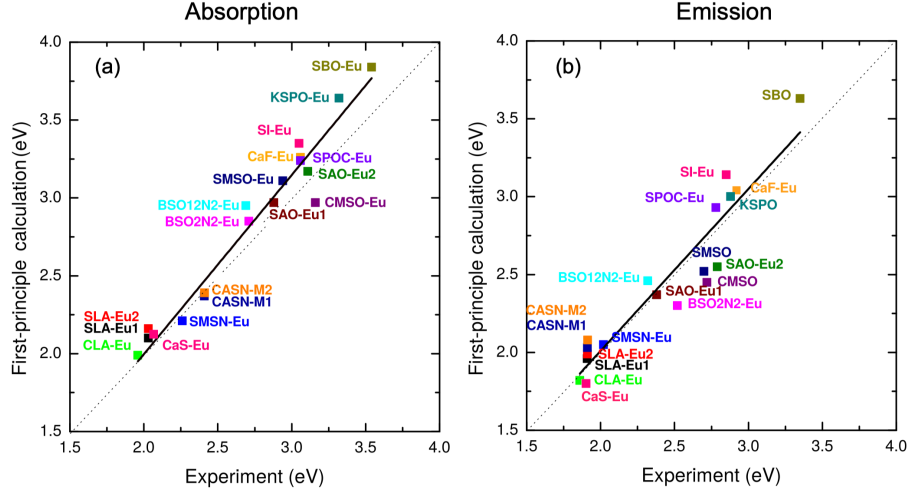


Figure 3.4: Comparison between experimental results and first-principles calculations for the (a) absorption energy and the (b) emission energy for a set of fifteen Eu^{2+} phosphors. Reproduced with permission from [77].

scopy, [78], and was based on the Hartree-Fock total energies at that time. Concerning density-functional theory, in 1976, Gunnarson and

Lundqvist [75, 79] proved a theorem stating that the DFT total energy of the ground-state of a particular (constrained) symmetry can be exactly obtained. However, the DFT exchange-correlation functional to be used is not the one of the unconstrained ground-state: a specifically tailored exchange-correlation functional should be used in the context of such exact theorem. In practice, no study of realistic materials has relied on such a specialized exchange-correlation functional, but all used the (unconstrained) ground-state one. In many cases, a truly predictive power resulted anyhow. Indeed the usage of the technique is pragmatic, and the results are nevertheless qualitatively and quantitatively helpful [80, 81]. The (constrained-occupation) Δ SCF approximate methodology, as we use it, can compete with several other approaches, like TD-DFT, for the prediction of excited state energies [82].

In the context of the luminescence of phosphors, a set of illustrative examples of the use of this method can be found in references [77, 83–87]. In particular, Jia et al. assessed the predictive power of the method for a set of fifteen Eu^{2+} phosphors, as shown on figure 3.4. They calculated an absolute error with respect to experiment on absorption and emission energies within 0.3 eV. In this work, we focus on the shape of the emission spectra that arises from the coupling with phonons and not on the precise location of these spectra along the energy axis. The excited state occupations are specific to the system under study. In the case of Eu^{2+} , one of the seven 4f electron of the spin-up channel is promoted to the next spin-up 5d energy state, as shown on figure 3.5. This figure makes also the link with the configuration coordinate model presented in chapter 1. One starts with a relaxed ground state (labeled A_g) with energy E_g . After the electron promotion (A_g^* and energy E_g^*), the difference in energy with the A_g state provides an estimation of the semi-classical absorption energy :

$$E_{\text{abs}} = E_g^* - E_g. \quad (3.1)$$

After structural relaxation, the relaxed excited state is found (state A_e^* with energy E_e^*), which allows one to compute the ZPL energy,

$$E_{\text{ZPL}} = E_e^* - E_g, \quad (3.2)$$

and the Franck-Condon relaxation energy of the excited state,

$$E_{\text{FC},e} = E_g^* - E_e^*. \quad (3.3)$$

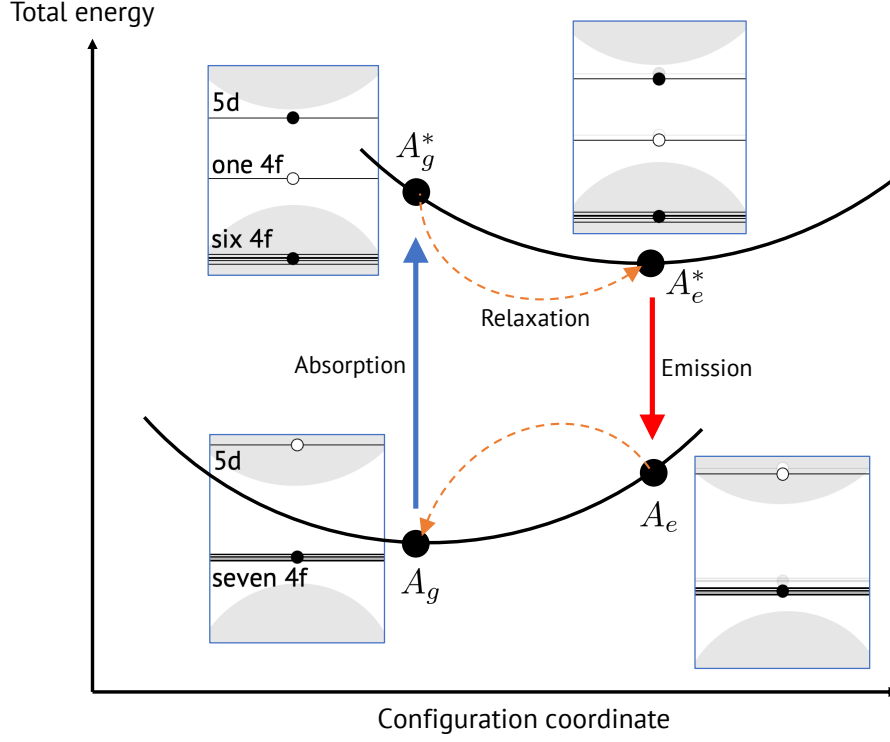


Figure 3.5: Schematic representation of the constrained occupation Δ SCF method, as used in this work for simulating the luminescent properties of Eu^{2+} phosphor.

De-promoting the electron with the relaxed atomic positions of the excited state (A_e with energy E_e) allows one finally to find the emission energy,

$$E_{\text{em}} = E_e^* - E_e, \quad (3.4)$$

and the Franck-Condon relaxation energy of the ground state,

$$E_{\text{FC},g} = E_e - E_g. \quad (3.5)$$

Assuming harmonicity, one can extract the effective frequencies of the ground or excited states as

$$\omega_{\text{eff}\{g,e\}}^2 = \frac{2E_{\text{FC},\{g,e\}}}{\Delta Q^2}, \quad (3.6)$$

with ΔQ obtained from equation 1.1. The corresponding Huang-Rhys factors can be obtained from equation 1.5.

This Δ SCF methodology has two clear advantages. First, there is in principle no additional computational cost with respect to a classical ground state computation. In practice, the SCF convergence is generally harder to reach, elongating the computational time. Second, one can perform an atomic relaxation with these constrained occupations just as a classical ground state relaxation. On the other hand, we note that this methodology works well for excited states that are well approximated by single-determinant states. Multi-determinant, or multi-degenerate excited states might be poorly reproduced.

Let us end this section with a comment on the level of theory used to describe the system under study with DFT. For "simple" defects (in the sense that there is no d or f electrons are at play) typically studied nowadays in the context of quantum technologies (NV center, SiC divacancy,...), it is now considered state of the art to use hybrid functionals [58, 59, 88, 89]. Although recently, it was shown that the SCAN meta-GGA functional [90] allows to almost reach the accuracy of the hybrid Heyd–Scuseria–Ernzerhof (HSE) functional for defect centers in diamond, at a lower computational cost [91].

On the other hand, defect transitions of lanthanides involving f electrons remain poorly studied with hybrids. To compute the photoluminescence of these system with the Δ SCF, it is still standard to rely on the DFT+U methodology [38, 77, 84–86, 92, 93], and this work is no exception. In the LDA (GGA) + U method [94, 95], the valence electrons are divided into two subsystems: (i) localized d (or f) electrons, where the Coulomb repulsion U is included through a Hubbard-like term in a specially tailored Hamiltonian, and (ii) delocalized s and p electrons, which are assumed to be adequately described by the standard orbital-independent one-electron potential in LDA or GGA.

Regarding the choice of U value, it is possible to stay in a fully ab-initio spirit and to determine self-consistently U based on linear response theory [96]. However, in this work, it is chosen to stay consistent with previous works [77, 97] and to use the same fixed values of U, determined by comparing experimental absorption and emission energies of various Ce^{3+} and Eu^{2+} phosphors (figure 3.4).

3.3 COMPARISON WITH WAVE-FUNCTION BASED METHODS

In the constrained-occupation Δ SCF method, the Kohn-Sham orbitals are optimized with non-Aufbau occupations that aim at mimicking the lowest state of the $4f^6 5d^1$ configuration. The whole $4f^6 5d^1$ configur-

ation, which gives rise to a complex fine structure in the absorption spectrum, cannot be captured with this method. However, because the emission involves the transition between the lowest state of the $4f^6 5d^1$ configuration and the $4f^7$ ground state (well reproduced with DFT), the Δ SCF technique is nevertheless suitable to model the emission.

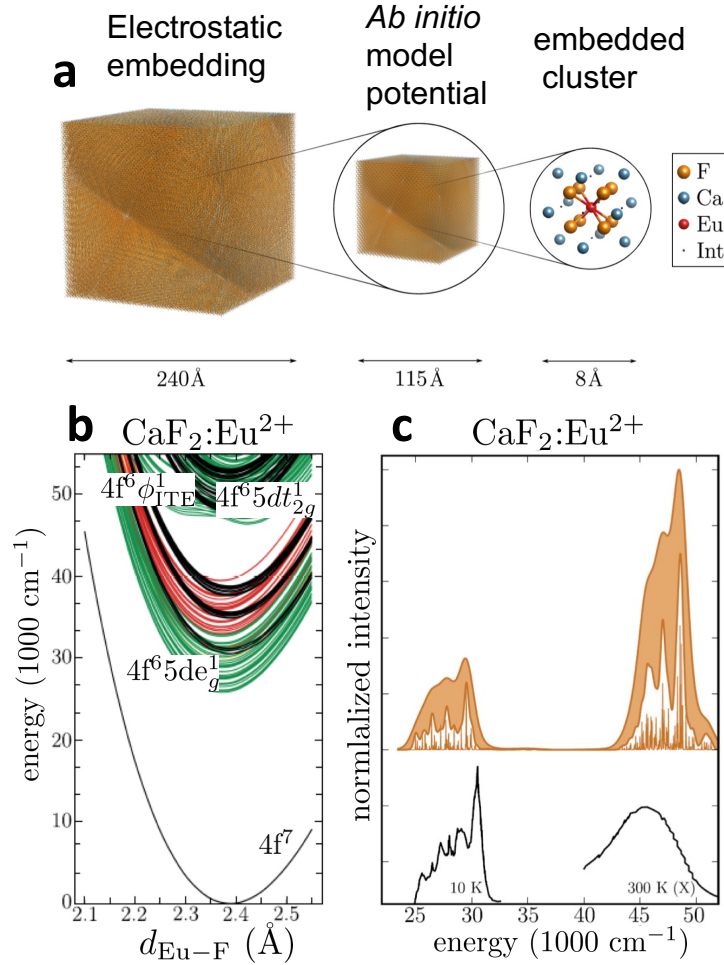


Figure 3.6: Multiconfigurational embedded cluster calculations to treat the Eu^{2+} excited states. (a) The system of interest is divided in an embedded-cluster region which is treated at the highest all-electron quantum-chemical level, a shell which is represented by the full-ion *ab initio* model potential and a thick layer of point charges (electrostatic embedding). (b) Potential energy curves for the $\text{Eu}^{2+} \text{CaF}_2$. The color represents the spin-character of the eigenstates, ranging from green for pure spin-octets to red for pure spin-sextets. (c) Computed $4f^7 - 4f^6 5d^1$ absorption spectrum compared to experimental absorption (bottom). Reproduced with permission from [98].

Another way to describe the lanthanides $4f^{n-1}5d^1$ excited state takes its theoretical roots from quantum-chemistry/wavefunction-based methods with multiconfigurational embedded cluster calculations, as the one used by Joos, Seijo and Barandiarán [98], and described recently in a book [99]. In such an approach, the system of interest is divided in an embedded-cluster region which is treated at the highest all-electron quantum-chemical level, a shell which is represented by the full-ion ab initio model potential (AIMP) [100] and a thick layer of point charges (electrostatic embedding), treated classically [101], to terminate the system, see figure 3.6 (a).

While we do not have experience with this technique, it is clear that such a method offers a much better description of the whole excited state landscape, as illustrated on figure 3.6 (b), which presents the crowded manifold of the Eu^{2+} excited states in CaF_2 . In particular, such analysis provides insightful results on the origin of the absorption bands in Eu^{2+} phosphors (figure 3.6 (c)) and, for instance, the origin of the ‘staircase’ pattern of the absorption band. However, given the available computational resources, this technique seems to be applicable only to an Eu environment with high local symmetry ($\text{CaF}_2\text{:Eu}$, CaS:Eu ,...) to reduce the computational load. Additionally, the vibronic interaction can only be treated in an approximate way : i.e. by computing the potential energy surface as a function of the Eu-ligand distance only, providing the so-called “breathing mode” vibrational frequencies. Hence, applying this technique to understand the complex vibronic side-band for the emission currently seems out of reach.

The main advantage of the constrained-occupation approach is precisely that it allows to perform a direct relaxation in the lowest excited state, allowing one to gain insights into the complex vibronic side-band appearing in emission spectrum.

Overall, the two approaches complement each other. The ΔSCF approach is useful to understand the vibronic interaction between the $4f$ and the lowest $5d$ excited state, limiting its predictive power to the emission band. The wave-function based approach is interesting to describe the electronic contribution of the absorption band and allows one to capture the complexity of the whole $4f^6 5d^1$ configuration, but with limited predictive power on the vibronic interaction. To our knowledge, there exists no study performing a careful comparison of the two methods for similar systems, but such bridge would constitute an interesting direction of research.

We note also the existence of recent studies of more complex phosphors with embedded cluster approaches using TD-DFT [102, 103]. Some studies [36, 104, 105] have used ground-state DFT results to parametrize ligand-field calculations. Such approaches typically offer a good description of the excited state landscape.

3.4 FORCES VERSUS DISPLACEMENTS

For a given phonon mode ν , the corresponding partial Huang-Rhys factor $S_\nu = \frac{\omega_\nu \Delta Q_\nu^2}{2\hbar}$ is computed thanks to the mass-weighted displacement, $\Delta R_{\kappa\alpha}$, between ground and excited states projected on this phonon mode:

$$\Delta Q_\nu = \sum_{\kappa\alpha} \sqrt{M_\kappa} \Delta R_{\kappa\alpha} e_{\nu,\kappa\alpha}, \quad (3.7)$$

where κ labels the atoms and α the cartesian direction. In the harmonic approximation, the phonon modes are computed by solving the generalized eigenvalue problem

$$M_\kappa \omega_\nu^2 e_{\nu,\kappa\alpha} = \sum_{\kappa'} C_{\kappa\alpha,\kappa'\alpha'} e_{\nu,\kappa'\alpha'}, \quad (3.8)$$

with the interatomic force constants (IFCs) $C_{\kappa\alpha,\kappa'\alpha'} = \frac{\Delta F_{\kappa'\alpha'}}{\Delta R_{\kappa\alpha}}$. With such definition, equation (3.7) can be rewritten as

$$\Delta Q_\nu = \frac{1}{\omega_\nu^2} \sum_{\kappa\alpha} \frac{\Delta F_{\kappa\alpha} e_{\nu,\kappa\alpha}}{\sqrt{M_\kappa}}. \quad (3.9)$$

It is hence equivalent (under the harmonic approximation) to work either with the displacements $\Delta R_{\kappa\alpha}$ caused by the electronic transition or with the non-equilibrium forces $\Delta F_{\kappa\alpha}$. For emission, these forces are the ones computed in the electronic ground state for the atomic positions of the relaxed excited-state (A_e state). The use of equation (3.9) is advantageous because it allows to increase the supercell size and hence minimize finite-size effects mentioned in the section on the supercell technique. Indeed, the forces $\Delta F_{\kappa\alpha}$ decay quickly to zero compared to the displacements with respect to the distance with the Eu substitutional defect as illustrated in figure 3.7 (a)-(b) in the case of $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$. It can be safely assumed that the forces computed within a small red supercell, see figure 3.7 (c), are already converged and without finite-size effect because of this short decay, and that the forces outside this supercell are essentially zero. This means that we can

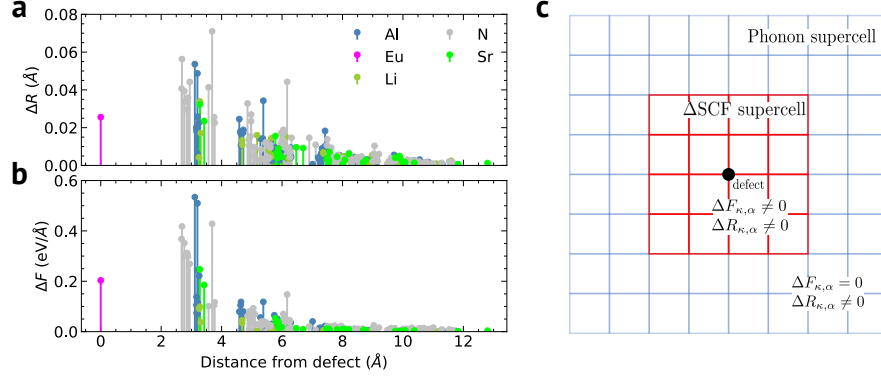


Figure 3.7: (a) Norm of the displacement induced by the 5d-4f transition for Eu(Sr₂) as a function of the distance from the Eu atom in Sr[LiAl₃N₄]:Eu²⁺ (b) norm of the forces in the 4f ground state at the 5d equilibrium atomic positions as a function of the distance from the Eu atom. The decay of forces is much faster than the decay of displacements. (c) Cartoon of a small red supercell containing the Eu(Sr) substitutional defect where the forces are the ones computed with DFT. Outside this red supercell, the forces are set to zero because of their short-range decay while the displacements are non-zero and are computed with the IFCs computed on this large blue supercell. Reproduced from [106].

use the forces computed on this red " Δ SCF" supercell, and deduce the displacements at much larger distances on the blue "phonon" supercell via the IFCs computed on this large supercell. The fact that the forces are set to zero beyond the red supercell does not imply that these atoms remain in their bulk positions, i.e., $\Delta R_{\kappa\alpha} \neq 0$. If the constraints were removed, these atoms would move to their equilibrium positions during a complete geometry optimization, as the movement of neighboring atoms in this process would generate a build-up of forces. This subtle point is actually directly included when using equation (3.9) on the blue supercell. Such observation, initially proposed by Alkauskas [58], allows to substantially increase the supercell size used in calculations, without explicitly computing the displacements in very large blue "phonon" supercells.

3.5 PHONON COMPUTATIONS OF DEFECT SYSTEM

Phonon modes are essential quantities that should be computed in order to obtain phonon-resolved luminescence spectra. These phonons should

be calculated within the “phonon” supercell, as described in section 3.4, if forces are being used instead of displacements. If displacements are used, the “phonon” supercell is identical to the “ Δ SCF” supercell, allowing phonon calculations to be performed on the same Δ SCF structure. The calculation of phonons requires the calculation of the Hessian of the potential energy surface, $C_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial E}{\partial R_{\kappa'\alpha'} \partial R_{\kappa\alpha}} = -\frac{\partial F_{\kappa'\alpha'}}{\partial R_{\kappa\alpha}}$, also known as the matrix of interatomic force constants.

In a periodic solid, the phonons eigenvectors $e_{\kappa\alpha,\nu}(\mathbf{q})$ and eigenfrequencies $\omega_{\mathbf{q}\nu}$ are typically obtained on a primitive cell at a given wave vector $\mathbf{q}$ by solving the eigenvalue problem :

$$\sum_{\kappa'\alpha'} \tilde{D}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) e_{\kappa'\alpha',\nu}(\mathbf{q}) = \omega_{\mathbf{q}\nu}^2 e_{\kappa\alpha,\nu}(\mathbf{q}). \quad (3.10)$$

The dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q})$ is connected to the interatomic force constants (IFCs) by

$$\tilde{D}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = \frac{1}{(M_\kappa M_{\kappa'})^{1/2}} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}). \quad (3.11)$$

where $\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q})$ is the Fourier transform of the real-space IFCs :

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = \sum_{p'} C_{\kappa\alpha,\kappa'\alpha'}^{p'0} e^{i\mathbf{q} \cdot \mathbf{R}_{p'}}, \quad (3.12)$$

with the real-space IFCs being written as

$$C_{\kappa\alpha,\kappa'\alpha'}^{p'} = \frac{\partial^2 E}{\partial \tau_{\kappa\alpha}^0 \partial \tau_{\kappa'\alpha'}^{p'}}. \quad (3.13)$$

$\tau_{\kappa'\alpha'}^{p'}$ is the position of the atom κ' in the unit cell p' , along the Cartesian direction α' . The second atom is chosen in the reference unit cell 0.

The presence of a defect in a lattice influences the phonon modes and their frequencies. The two primary types of alterations caused by this are the emergence of local modes and in-band resonances [54]. In both cases, the mode amplitude near the defect is significantly modified. Local modes are most commonly associated with light imperfections, resulting in mode frequencies that are higher than those found in perfect crystals. True local modes, where the vibration amplitude quickly diminishes to zero away from the defect, can also occur at frequencies within gaps in the perfect crystal spectrum. In-band resonances (also called quasi or pseudo local modes [58]) occur at frequencies within the perfect crystal spectrum and affect a range of modes. They are

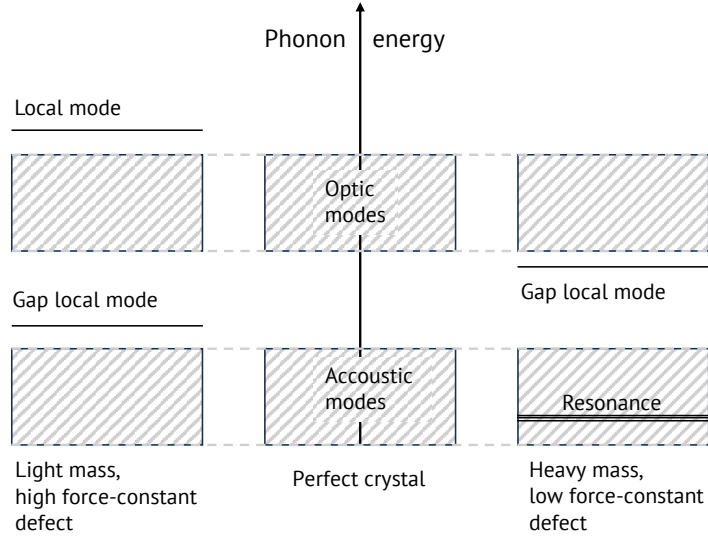


Figure 3.8: Local and resonant phonon modes brought by a defect in a perfect lattice. The diagram shows various possibilities for different defect masses and force constants. Inspired by [54].

observed in cases of heavy atom impurities and defects that are weakly coupled to the host lattice. Figure 3.8 illustrates the various forms of local modes and resonances for different defect masses and force constants.

Now that we have qualitatively discussed the impact of impurities on phonons, we can see how these phonons can be computed using Density Functional Theory (DFT). Two main computational techniques are commonly used to evaluate phonons in solids with DFT.

FINITE-DISPLACEMENTS Also called "frozen phonon", such method obtains the DFT forces (efficiently obtained through the Hellman-Feynman theorem [107, 108]) and calculates the derivatives of the forces via finite difference. The force constants are determined using a sufficiently large sample of supercells, each with various displacement configurations and corresponding forces derived from first-principles calculations. Phonons are computed directly (without interpolation) from the supercell force constants at the wave vectors commensurate with the supercell shape with respect to the primitive cell. For other wave vectors, phonons are obtained through interpolation. In this work, the automation of the involved computational steps is done with the Phonopy code [109, 110]. The main benefits of this method are its

simplicity and ease of implementation, making it compatible with any electronic structure method capable of calculating forces. This includes semilocal-DFT, hybrid-DFT, or other non-DFT approaches such as force fields or dynamical mean-field theory. However, a drawback of this method is that it necessitates the creation of large supercells to capture long-wavelength phonons, which can increase the computational cost.

DENSITY FUNCTIONAL PERTURBATION THEORY In the Density functional perturbation theory (DFPT) approach [111–115], force constants are precisely calculated in reciprocal space at arbitrary wave vectors by computing directly the variations of Kohn–Sham orbitals (Sternheimer equation). Additionally, force constants in direct space, similar to the supercell force constants of finite difference, can be computed by applying a Fourier transform to the reciprocal-space force constants sampled on a regular grid [114]. These direct-space force constants are then Fourier interpolated back into reciprocal space at arbitrary wave vectors.

The advantage of DFPT is that it eliminates the need to construct supercells, allowing for the calculation of a finite wave vector response within the primitive cell, which reduces computational costs compared to the finite displacement method. This makes it the preferred approach for obtaining dense sampling of wave vectors in reciprocal space. However, the downside of DFPT is that it is typically only available for DFT with semi-local functionals, as its implementation is more complex than in the finite difference method. Additionally, memory requirements can be high for large cells.

3.5.1 IFCs embedding approach

In the computation of the partial Huang-Rhys factors, one would like to obtain the phonons in very large supercells at wave vector $\mathbf{q} \rightarrow (0,0,0)$ (Γ point), so that the coupling with long-wavelength phonons is correctly captured. One would also like to include the coupling with (localized) phonons modes introduced by the defect. A direct approach, either with DFPT or finite difference, is not computationally attractive. Indeed, DFPT is best used for small pristine primitive cells at dense $\mathbf{q}$ -mesh (which corresponds to large pristine supercells after a folding procedure), while finite difference, for which the introduction of defect does not cause problem, remains costly for large supercells. One way to include both the defect effect (local modes) while converging long-

wavelength phonons is to employ the IFCs embedding approach [58, 59, 116–118].

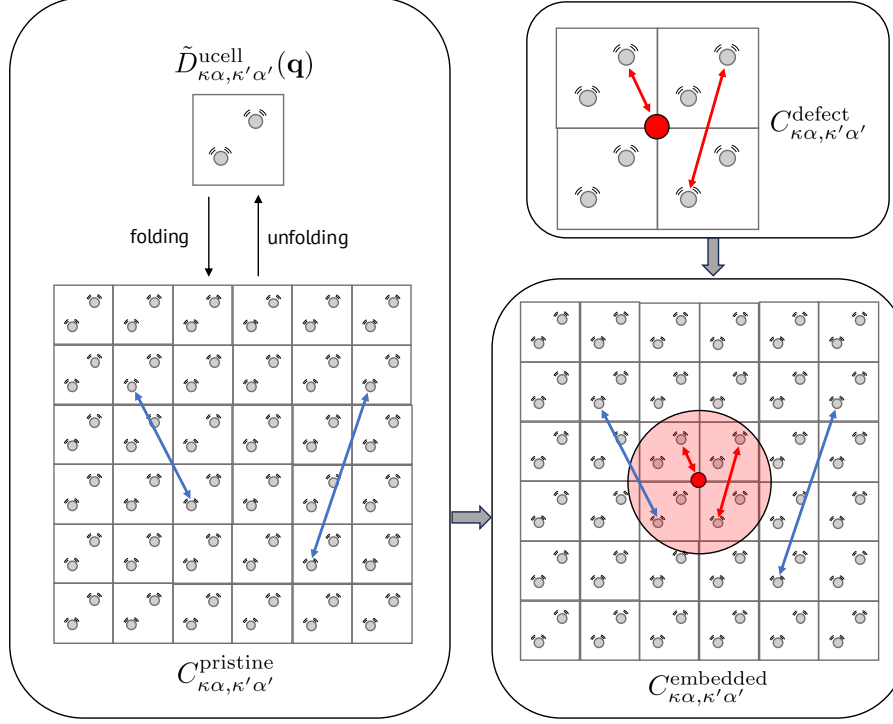


Figure 3.9: Schematic view of the interatomic force constants (IFC) embedding approach to obtain defect phonons in large supercells. Each arrow represents an IFC between a pair of two atoms. See text for details.

The procedure, illustrated in figure 3.9, is as follows:

First, the real-space interatomic force constants (IFCs) of the defect system, denoted as $C_{\kappa\alpha,\kappa'\alpha'}^{\text{defect}}$, are computed within a relatively small supercell (typically with a few hundred atoms). This is often done using a finite difference approach on the supercell at the Γ point, though Density Functional Perturbation Theory (DFPT) could also be employed if the memory requirements are manageable and/or if the level of theory required to describe the defect (e.g., DFT+U) is supported by the DFPT code.

Second, the IFCs of the pristine system, $C_{\kappa\alpha,\kappa'\alpha'}^{\text{pristine}}$, are obtained within a much larger supercell (typically with a few thousand atoms). A practical approach is to use DFPT on the unit cell to calculate the dynamical matrix on a $\mathbf{q}$ -mesh, potentially followed by Fourier interpolation to

obtain the matrix on a denser $[N_x, N_y, N_z]$ $\mathbf{q}$ -mesh. The information in the dynamical matrix, computed on a unit cell for a dense $[N_x, N_y, N_z]$ $\mathbf{q}$ -mesh, is equivalent to that in a dynamical matrix for a $[N_x, N_y, N_z]$ supercell at $\mathbf{q} = [0, 0, 0]$ (the Γ point). Mapping a $\mathbf{q}$ -mesh to $\mathbf{q} = [0, 0, 0]$ is referred to a folding procedure, and yields the pristine IFCs $C_{\kappa\alpha, \kappa'\alpha'}^{\text{pristine}}$.

Third, an embedded IFC matrix $C_{\kappa\alpha, \kappa'\alpha'}^{\text{emb}}$ is constructed using the following rules: If both atoms κ and κ' are within a sphere centered around the defect, with a cut-off radius R_c , then $C_{\kappa\alpha, \kappa'\alpha'}^{\text{emb}}$ is set to $C_{\kappa\alpha, \kappa'\alpha'}^{\text{defect}}$. For all other atomic pairs, the embedded IFC is set to the pristine value: $C_{\kappa\alpha, \kappa'\alpha'}^{\text{emb}} = C_{\kappa\alpha, \kappa'\alpha'}^{\text{pristine}}$. The cut-off radius R_c is typically determined by the size of the initial supercell used to compute the defect IFCs. Additionally, one could use a second cut-off radii R_b . If two atoms are not within a sphere of radii R_b , the IFC is set to zero. The use of this second cut-off has been used in some studies [59, 117] in order to obtain large sparse matrices, for which dedicated techniques allows faster diagonalization, see for instance reference [117]. In this work, we do not use this second cut-off. Overall, the whole procedure can break the acoustic sum rule

$$C_{\kappa\alpha, \kappa\alpha} = - \sum_{\kappa' \neq \kappa} C_{\kappa\alpha, \kappa'\alpha'}. \quad (3.14)$$

To correct for this, we follow the approach proposed in reference [117] and we set:

$$C_{\kappa\alpha, \kappa\alpha}^{\text{emb}} = - \sum_{\kappa' \neq \kappa} C_{\kappa\alpha, \kappa'\alpha'}^{\text{emb}}. \quad (3.15)$$

For the treatment of the Born effective charges (BECs), if the BEC of the substituted atom was computed in the defect phonon calculation, it is replaced by the BEC of the dopant atom. If not, one can choose to use the most common oxidation state of the dopant atom as its new BEC. The same approach applies to interstitials, but in this case, the dopant atom and its corresponding BEC are simply added. For vacancies, the atom and its BEC are removed.

Diagonalizing this embedded IFCs provides the phonon modes of a defectuous $[N_x, N_y, N_z]$ supercell, where the defect effect on the IFCs was included through the embedding procedure.

In recent years, machine-learned interatomic potentials (MLIPs) such as MACE [119] or CHGNet [120] have emerged as a promising alternative to traditional methods for calculating phonon properties, including the defect phonons described here. MLIPs are trained on high-quality reference data, such as density functional theory (DFT)

calculations, and can provide a computationally efficient way to model large systems with defects. Once trained, MLIPs can be used to compute defect-induced phonons in large systems, potentially reducing the computational cost compared to DFPT or finite difference methods. Although MLIPs have shown great potential, their accuracy and generalizability depend on the quality of the training data and the specific type of defect being studied. Nonetheless, they offer an exciting avenue for future research, particularly in systems with complex defects or in cases where very large supercells are needed.

3.5.2 Quantifying a phonon mode localization

The localization of the phonon modes can be characterized by computing the inverse participation ratio (IPR) defined as [38, 58, 59]

$$\text{IPR}_\nu = \frac{1}{\sum_{\kappa} |\langle \mathbf{e}_{\nu,\kappa} | \mathbf{e}_{\nu,\kappa} \rangle|^2}, \quad (3.16)$$

which indicates, roughly speaking, the number of atoms that participate to a phonon mode ν . For example, $\text{IPR}_\nu = 1$ means that only one atom vibrates and therefore the phonon mode is maximally localized, while $\text{IPR}_\nu = N$ means that N atoms vibrate in the supercell with the same amplitude.

The localization ratio β_ν is defined by taking the ratio of the total number of atoms in the supercell N and the IPR, $\beta_\nu = N/\text{IPR}_\nu$ where $\beta_\nu \approx 1$ represents a bulk-like delocalized mode while $\beta_\nu \gg 1$ corresponds to a quasi-local or local mode.

3.5.3 Example : local mode in the diamond split-interstitial

To illustrate the methodology, the split-interstitial defect in diamond is used as a toy model. A single isolated carbon interstitial in diamond has never been observed and is considered unstable. When it interacts with a regular diamond lattice, a “split-interstitial” forms, a defect where two carbon atoms share a lattice site and are covalently bonded with the neighboring carbon atoms, as shown on figure 3.10 (a). This defect has been extensively studied using electron paramagnetic resonance (R2 center) [121] and optical absorption [122]. Unlike most other defects in diamond, it does not produce photoluminescence. Still, the fact that the split-interstitial is linked by a stiffer sp^2 bond (instead of sp^3) produces an interesting local phonon mode involving the stretching of

the C-C pair with frequency well above the bulk phonon frequencies of diamond.

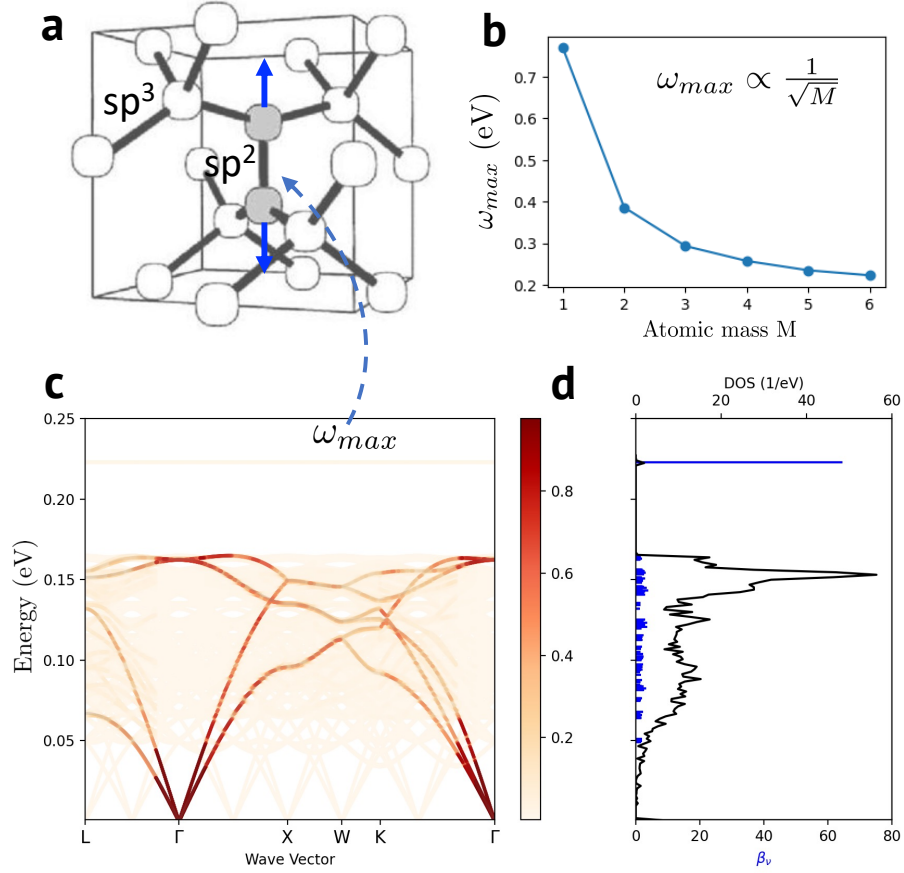


Figure 3.10: (a) Structural model of the carbon split-interstitial in diamond. The blue arrows represents the local stretching mode of the split-interstitial. (b) Variation of the frequency of such mode as the mass of the atoms composing the split-interstitial varies. (c) Unfolded phonon band structure of a diamond defectuous supercell, obtained after an IFCs embedding procedure. (d) The corresponding phonon density of states (black), with the individual localization ratios β_v of each phonon mode (blue).

The IFCs of a large pristine supercell of diamond and of a smaller defectuous supercell are computed. The embedded phonons are then obtained following the above-mentioned procedure. An unfolding technique [123] allows an interesting visualization of these defect phonons. It allows to draw a phonon band structure of an imperfect lattice (defectuous supercell, an alloy system modeled with a supercell,...) onto the

wave vector path of the underlying pristine unit cell. It can be linked with a spectral function where the weights indicate how similar is a state in the defect supercell to a Bloch state in the underlying unit cell. For relevant equations and discussions about such technique, the reader is referred to references [109, 123] or to [124, 125] for alloy compounds. The implementation of the Phonopy code, described in reference [109], is used in this work.

The result for the split interstitial is shown on figure 3.10 (c), with a colormap that represents the unfolding weights. One clearly recognizes the slightly perturbed phonon band structure of the perfect C-diamond structure. In addition, a flat band (local mode) with frequency ω_{max} is found above the bulk frequencies and corresponds, as expected, to the stretching of the split-interstitial. It is interesting to vary in the simulation the atomic mass M of the two atoms composing the split interstitial. From a C-C to a H-H pair, one finds that the local mode frequency nearly follows an expected $1/\sqrt{M}$ relationship, as depicted on figure 3.10(b). Finally, one can compute the localization ration β_v of each mode. They are presented in blue on figure 3.10 (d), alongside the phonon density of states.

3.6 CONVERGENCE OF THE HUANG-RHYS SPECTRAL FUNCTION

As demonstrated in chapter 2, the lineshape function is determined entirely by the Huang-Rhys spectral function, making it the most critical quantity to carefully converge with respect to relevant computational parameters. The convergence behavior is system-dependent and varies based on the underlying physics; for some systems, a supercell with 200 atoms might yield reasonable results, while others may require up to 2000 atoms for accurate convergence.

In certain cases, the embedding methodology does not significantly alter the spectral function compared to the phonons of the pristine system alone, particularly when the electronic transition does not strongly couple with defect phonon modes. However, for other systems, considering the defect effect on phonons can provide new insights.

Additionally, whether forces or displacements are used in the calculations may yield different results, especially if the system is not well-described by the harmonic approximation.

For further examples of in-depth convergence studies, readers may refer to the NV center in reference [58] or defects in SiC [59]. In this chapter, we provide an example involving the Eu^{2+} impurity in SrCl_2 ,

which highlights the challenges of achieving strict convergence in the low-frequency region of the spectral function due to the coupling with long-wavelength phonons.

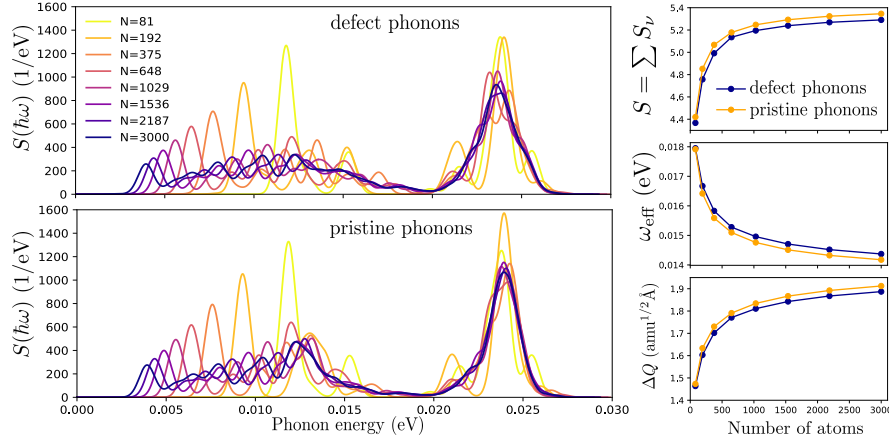


Figure 3.11: Convergence of the Huang-Rhys spectral function as a function of the size of the large phonon supercell in $\text{SrCl}_2:\text{Eu}^{2+}$, for defect phonons obtained with the embedding methodology (up) and for pristine phonons (down).

Figure 3.11 presents a convergence study of the Huang-Rhys spectral function as a function of the size of the large “phonon” supercell. The largest cut-off radius R_c for the IFCs embedding, as illustrated in figure 3.9, is 7.4 Å, which corresponds to a $3 \times 3 \times 3$ supercell. This means that within a 7.4 Å radius from the Eu^{2+} atom, the IFCs from the defect system are used (with the acoustic sum rule being applied afterward).

The results, shown in figure 3.11, include supercell sizes ranging from [3,3,3] (81 atoms) to [10,10,10] (3000 atoms). While the coupling with optical modes remains relatively stable (with same frequency positions, though the peaks broaden as the supercell size increases), a significant shift is observed in the low-frequency peak. This shift indicates the coupling with low-frequency phonons of long wavelengths. In fact, the atomic displacements caused by the 5d-4f transition in $\text{SrCl}_2:\text{Eu}^{2+}$ exhibit a very slow decay relative to the distance from the Eu atom. Such long-range displacements pattern couples with acoustic branch modes that have smaller wavevectors (or longer wavelengths) as the supercell size increases, as illustrated in figure 5.4 for the SALON phosphor case. The Huang-Rhys spectral function is also shown for

the scenario where only pristine phonons are considered ($R_c = 0$). No significant difference is observed in this system, mainly because the Eu atom remains static after the electronic transition. One can try to fit the ΔQ to extrapolate ΔQ to an infinite number of atoms N . With a fitting function of the form :

$$\Delta Q(N) = \Delta Q_\infty + b \left(\frac{1}{N} \right)^c, \quad (3.17)$$

the best fit is found for $\Delta Q_\infty=2.092$, $b=-2.522$, $c=0.315$.

Similar convergence studies for the Eu^{2+} impurity in other host structures can be found in the corresponding chapters.

3.7 LIMITS OF THE METHODOLOGY

Before finishing this chapter, we discuss below a list of limits and comments related to the methodology used. We distinguish between limits related to the luminescence lineshape theory itself (Huang-Rhys theory, chapter 2) and limits related to the use of DFT with plane waves and boundary conditions to obtain the parameters of the Huang-Rhys theory (chapter 3). Such summary is important to assess the domain of applicability of the methodology used. Also, when simulation and experiment disagree, it provides possible directions to look at to explain the discrepancies.

THEORY

- The formulation of the Fermi's golden rule (eq 2.9) is valid for molecules (with refractive index $n_D = 1$) or for solids with homogeneous and isotropic screening, but it is an approximation for 3D materials where the screening is more complex, and even more for 2D materials. Recently, a many-body perturbation theory framework allowed to go beyond that and study exciton-phonon coupling to predict the luminescence of the negatively charged boron vacancy in 2D hexagonal boron nitride [126]. This study also goes beyond the FC approximation. However, only one-phonon replica peaks were considered. The multi-phonon processes, within a many-body Green's function approach, can be obtained with a generalized cumulant formulation for neutral excitation spectra, by calculating of the out-of-equilibrium polarizability which gives access to the photo-luminescent spectrum

[127]. This paper also proposes an interesting connection between the many-body formulation and the Huang-Rhys formulation, see equations (30) and (31) therein.

- In the Huang-Rhys theory, it is assumed from the start that the dipole moment is not impacted by a change in the atomic structure (Franck-Condon approximation). One might go beyond that and include first-order corrections with respect to the configuration coordinate Q (Herzberg-Teller terms). Such analysis has been conducted for a few defects in diamonds and SiC [59], following an one-dimensional effective phonon mode model. It has been shown that the correction is very small in these systems.
- We work under the harmonic approximation, and the phonons of the electronic excited and ground states are supposed to be the same, except for a rigid shift ΔQ_v (we have a set of $3N$ displaced harmonic oscillators). This is because, within the Huang-Rhys theory, the computation of the spectra relies on the linear theory of electron-phonon coupling. Including quadratic terms in the multi phonon modes treatment would increase substantially the complexity of an already complex problem. To our knowledge, there exists no study assessing the validity of this approximation in solids, and it has always been validated *a posteriori* by verifying the agreement between simulation and experiment.

DFT

- The defect structure given to the DFT code might sometimes not be the same than the "real-life" defect structure. Often overlooked, a strong disagreement between theory and experiment might be caused by an incorrect identification of the defect center responsible for luminescence.
- The excited state is described with the standard Δ SCF approach, which often yields good results, even though using constrained orbital occupations in DFT does not have the same theoretical support as the calculation of the ground state. Comparison with more rigorous many-body approaches (but much more computationally intensive), or with wave-function based methods would be of great interest.
- Drawing conclusions from calculations performed using a too small supercell size might be dangerous, especially in (1) the

understanding of the coupling with phonons. Indeed, a too small size could lead to the coupling with artificial local modes, and to the absence of coupling with long-wavelength phonons. A convergence study with respect to this "phonon" supercell size is critical here. And (2) if the displacements induced by the electronic transition extend far from the defect. A convergence study with this " Δ SCF" supercell size is important, although the use of the forces permits to bypass this issue. It is noted that an effective phonon mode treatment (no phonon computation) often provides a good approximation of the global luminescent lineshape, and some of its important characteristics (maximum peak position, width,...).

CODE DEVELOPMENTS

This chapter presents a description of the Python package, which I developed as part of my doctoral research, that are designed to facilitate the computation of phonon-resolved luminescence spectra of defects in inorganic solids. It is integrated in the Abipy code to automate and post-process ABINIT computations. The following is written in the spirit of publishing a related publication in the Journal of Open Source Software (JOSS), tentatively entitled : *Bouquiaux et. al*, "Simulating complex phonon-resolved luminescence spectra of defects made simple with the "Lumabi" software. "

4.1 SUMMARY

Lumabi is a Python package integrated within the Abipy framework [128] designed to automate and streamline the computation of phonon-resolved luminescence spectra of defects in inorganic solids using the ABINIT density functional theory software [128–131]. The package addresses the growing need for efficient, reproducible workflows in materials science [132, 133], particularly in the study of defect-related luminescent properties, which are critical for applications ranging from quantum technologies [66, 134] to down-conversion phosphors materials used in white light LEDs [12, 15, 24]. Lumabi automates key steps in the computational workflow, from initial Δ SCF DFT calculations with constrained occupations, to the generation of defect phonons mode in large supercells, right through the final generation of luminescence spectra based on the Huang-Rhys theory [46, 59]. Tutorials and examples,

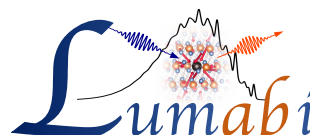


Figure 4.1: Lumabi logo.

written in the form of Jupyter books, can be found at this link : https://jbouquiaux.github.io/lumi_book/intro.html.

4.2 STATEMENT OF NEED

The study of defect-induced luminescence in materials is crucial for understanding and designing materials with specific optical properties. However, the computational workflow required to accurately predict these properties is complex and often labor-intensive, involving multiple-stage DFT calculations, phonon computations, and post-processing.

Given such importance of defects in materials and the complexity of the involved workflow to simulate them, a number of software packages have been developed to manage the pre- or post-processing of general defect calculations [135–142]. The few that focus on luminescent properties [143–145] are all interfaced with commercial software VASP [146], and only provide the post-processing part of DFT computations following the formalism proposed by Alkauskas et al. [58]. Also, the generation of defect phonons mode in large supercells following an embedding of the interatomic force constants is currently not available in any software to our knowledge.

Divided in four main Python modules, Lumabi provides a solution to automate all the necessary tasks to compute phonon-resolved luminescence spectra of defects. The DFT computations are performed with the open-source ABINIT software [128–131]. The generation of ABINIT input files, the automatic workflow management, and the post-processing work are done with the help of the Abipy package, which is interfaced with Pymatgen [147]. The code is interfaced with the Phonopy [110, 148] package for the phonon-related tasks. This tool is suited for researchers looking for accurate simulations of defect luminescence with limited human intervention.

4.3 SOFTWARE DESCRIPTION, FEATURES, AND COMPUTATIONAL WORKFLOW

The code is structured around four main Python modules, each handling a different stage of the computational workflow. While these modules are designed to be used seamlessly, the output of one providing the input of the next, the individual building blocks can be used independently with ease. We describe here the overall working principles

of each block. For a more practical approach, it is suggested to follow the [online tutorials](#) of the different modules and related examples.

LumiWork Module (Abipy/flows/lumiwork.py)

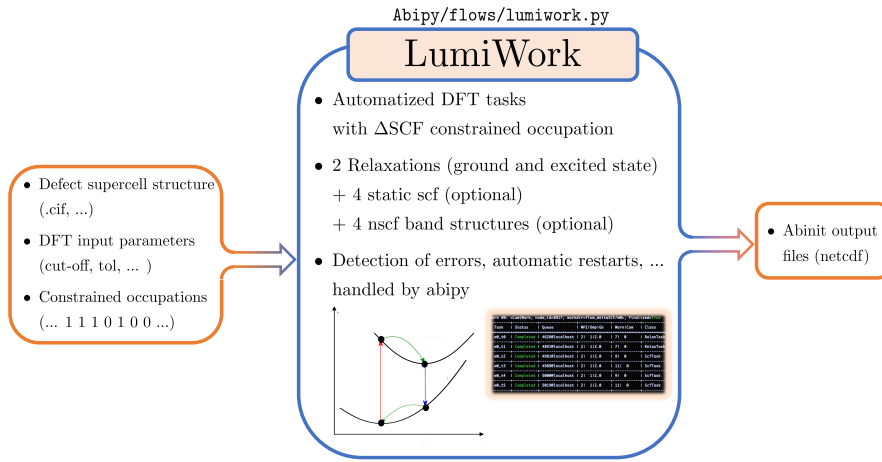


Figure 4.2: The LumiWork module, an AbiPy Workflow that automates ABINIT DFT tasks with Δ SCF constrained occupations.

A computational workflow to compute phonon resolved PL spectra of defect system typically begins with the LumiWork module (see figure 4.2), which automates ABINIT DFT tasks with Δ SCF constrained occupations [75, 76]. Users input the defect supercell structure (e.g. a cif file), DFT parameters (e.g., plane-wave cut-off, stopping SCF criterion,...), and constrained occupations of the Kohn-Sham states that aim at mimicking the excited state of the system under study. This module manages two structure relaxations, for both the ground and excited states and offers optional single-shot static SCF and non-SCF band structure calculations. Note that the workflow is dynamic : the relaxed excited state is not known in advance, which requires the creation of inputs at run-time.

The LumiWork class inherits from the Work Abipy class. Hence, it benefits from the error detection and automatic restarts handling available for all ABINIT-related Works (such as an approaching time limit constrained by a job manager, or an unconverged task). This ensures that most of the computations proceed smoothly without interruptions.

The important outputs from this module are in netcdf format, which serve as the basis for subsequent modules.

Δ SCF Post-Processing Module (Abipy/lumi/deltaSCF.py)

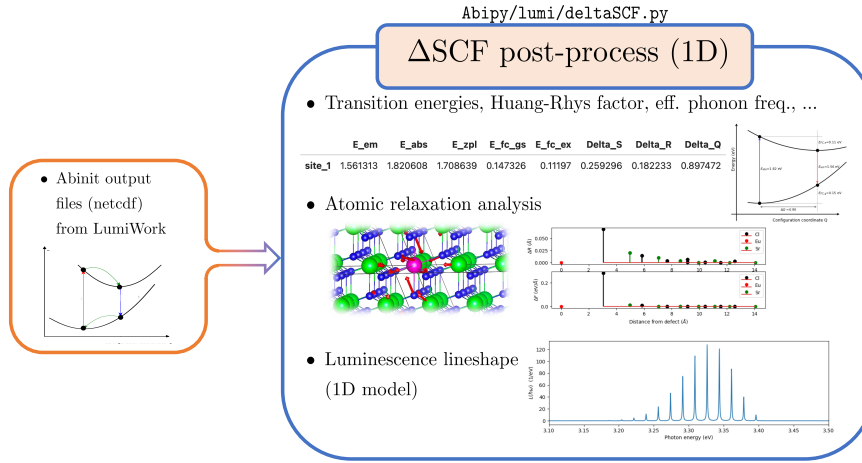


Figure 4.3: The Δ SCF module, designed to post-process Δ SCF constrained occupations calculations using a one-dimensional configuration coordinate model.

The next step in the workflow is handled by the Δ SCF post-processing module, shown schematically in figure 4.3. This tool takes the netcdf output files from the previous LumiWork module and processes them following a one-dimensional configuration coordinate model (see references [73, 77] or equations of section 3.2 of the present thesis). This analysis provides detailed insights into the luminescence characteristics of the defect under study, computing properties such as transition energies, Huang-Rhys factors, effective phonon frequencies, and lineshapes following this 1D model or within a semi-classical approximation (see equations 1.6 and 1.8). It is also able to help in the analysis of the atomic relaxation (generating for instance automatic VESTA [149] files with relaxation vectors). In the case of experimental lineshapes with resolved phonon peaks, it is important to note that the lineshapes obtained from this tool *are not* supposed to present a good agreement with experimental lineshapes at the level of the phonon peaks. Indeed, the model only considers a single effective phonon frequency ω_{eff} , and

one should use the next modules to obtain a better agreement. Still, the 1D model is able to give the global spectrum shape, or the total Huang-Rhys factor, which can be compared to experiment.

IFCs Embedding Module (*Abipy/embedding/embedding_ifc.py*)

The Interatomic Force Constants (IFCs) Embedding module has the role to calculate defect phonons in large supercells at the $\mathbf{q} = (0,0,0)$ (Γ point) wave vector. This module addresses the computational challenges associated with capturing both the coupling with long-wavelength phonons and the localized phonon modes introduced by defects. Direct methods, such as Density Functional Perturbation Theory (DFPT) [114] and finite difference approaches [148], are impractical for large supercells due to their high computational costs. First employed in the context of the luminescence of the NV center by Alkauskas et al. [58], it has been then used in various other systems [59, 91, 106, 117, 150]. The procedure relies on the short-range nature of interatomic forces to build IFCs matrices for defect supercells containing thousands of atoms, targeting the dilute limit.

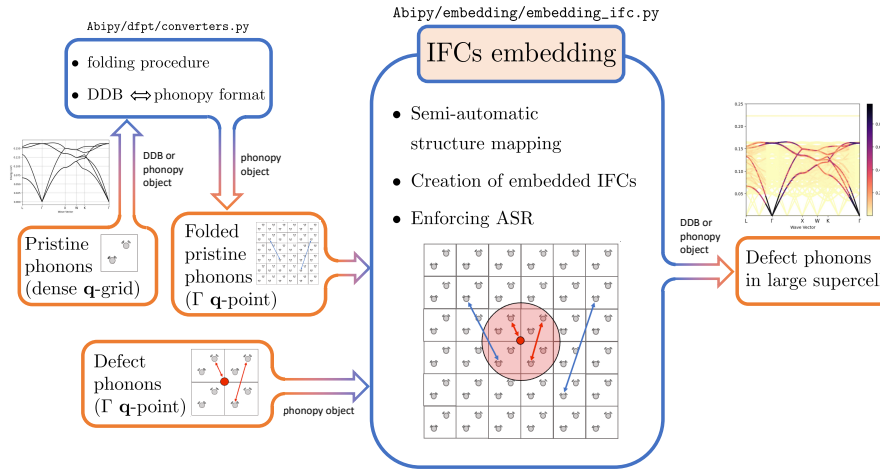


Figure 4.4: The IFCs embedding module, allowing to calculate defect phonons in large supercells.

First, the real-space interatomic force constants (IFCs) for the defect system $C_{\kappa\alpha,\kappa'\alpha'}^{\text{defect}}$ are computed within a relatively small supercell. Typic-

ally, this is achieved using a finite difference approach at the Γ point using Phonopy.

Second, the IFCs of the pristine system $C_{\kappa\alpha,\kappa'\alpha'}^{\text{pristine}}$ are computed in a much larger supercell. A practical approach involves using DFPT on the unit cell to calculate the dynamical matrix across a $\mathbf{q}$ -mesh. This is often followed by Fourier interpolation to obtain a denser $\mathbf{q}$ -mesh, equivalent to a large supercell at the Γ point. This folding procedure yields the pristine IFCs $C_{\kappa\alpha,\kappa'\alpha'}^{\text{pristine}}$. Such folding is implemented, and receives as input an ABINIT DDB file (or a phonopy object) and output a Phonopy object containing the folded pristine phonons.

Third, an embedded IFC matrix $C_{\kappa\alpha,\kappa'\alpha'}^{\text{emb}}$ is constructed using the following rules: If both atoms κ and κ' are within a sphere centered around the defect, with a cut-off radius R_c , then $C_{\kappa\alpha,\kappa'\alpha'}^{\text{emb}}$ is set to $C_{\kappa\alpha,\kappa'\alpha'}^{\text{defect}}$. For all other atomic pairs, the embedded IFC is set to the pristine value: $C_{\kappa\alpha,\kappa'\alpha'}^{\text{emb}} = C_{\kappa\alpha,\kappa'\alpha'}^{\text{pristine}}$. The cut-off radius R_c is typically determined by the size of the initial supercell used to compute the defect IFCs. Additionally, one can use a second cut-off radii R_b . If two atoms are not within a sphere of radii R_b , the IFC is set to zero. This allows one to obtain a sparse matrix, for which faster diagonalization techniques may be used, although the current implementation does not natively support such technique. Finally, the Acoustic Sum Rule is reinforced, following the conventions of reference [59]. The code performs a mapping between the structures of the pristine and defect computations. Such mapping is not trivial because the atomic positions of the defect supercell might not be the same as the pristine positions. Also, vacancies or interstitials should be handled with care during the mapping. For this reason, the mapping is done in a semi-automatic way, meaning that the user is responsible for the input of the different structure manipulations needed to go from the pristine cell to the defect cell. For details about this mapping, several examples are provided with the code. In the end, a Phonopy object containing the embedded IFCs and the new large defect supercell structure is created. For the treatment of the Born effective charges (BECs), if the BEC of the substituted atom was computed in the defect phonon calculation, it is replaced by the BEC of the dopant atom. If not, one can choose to use the most common oxidation state of the dopant atom as its new BEC. The same approach applies to interstitials, but in this case, the dopant atom and its corresponding BEC are simply added. For vacancies, the atom and its BEC are removed.

Lineshape Calculation Module (*Abipy/lumi/lineshape.py*)

As a final step, the Lineshape module is used. The main task of this module is to compute the Huang-Rhys spectral function $S(\hbar\omega)$ [58, 106], and to generate temperature-dependent photoluminescence (PL) spectra using the efficient generating function approach [59]. The mathematical formalism can be found in the chapter 2 of the present thesis. The code expects as inputs the zero-phonon line energy, the atomic displacements $\Delta R_{\kappa\alpha}$ or forces $\Delta F_{\kappa\alpha}$ induced by the electronic transition (conveniently obtained from the Δ SCF post-process block), and the phonon modes as a Phonopy object (potentially obtained from the IFCs embedding module). Notice that the use of the displacements is only compatible if the phonon supercell is of the same size as the Δ SCF supercell. The use of the forces (equivalent under the harmonic approximation) allows one to use efficiently the previous block and enlarge the supercell size, ensuring a proper convergence of the Huang-Rhys spectral function, see section 3.4 or references [58, 59, 106]. An analysis of the different phonon modes localization can also be performed.

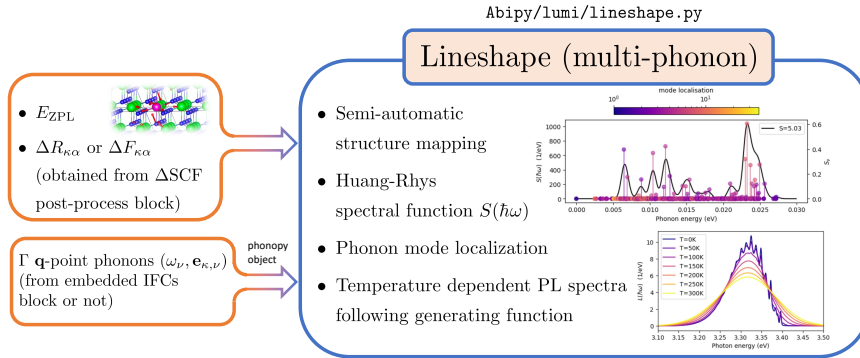


Figure 4.5: The lineshape module, allowing to compute the temperature-dependent spectra.

EXAMPLES AND APPLICATIONS

This computational workflow has been used mostly for inorganic phosphors activated with Eu^{2+} defects [73, 106], but it has been tested for other systems such as the F-center (oxygen vacancy) in CaO or the NV center in diamond, and it is able to deal in principle with any kind of point defect. Examples of use can be found in the example sections of

the [online tutorial](#). The results presented in this work were obtained with this tool, and the reader is referred to the different result sections for examples of applications.

A THEORETICAL PERSPECTIVE ON THE NARROW EMISSION IN EU-DOPED UCr_4C_4 PHOSPHORS

In the two following chapter, I present the results of computational investigations conducted on seven phosphor materials, focusing on their luminescent properties. These materials have been selected either for their technological relevance to phosphor-converted white light-emitting diodes, and/or theoretical relevance because of their clear vibronic features (resolved phonons peaks in their photo-luminescence spectrum). The methodology applied follows the theoretical framework outlined in previous chapters, which is based on the multi-phonon mode Huang-Rhys model (chapter 2), fed by Density Functional Theory (DFT) calculations (chapter 3) and assisted by the "Lumabi" pre and post-processing code developped during this thesis (chapter 4). The hope is to provide with these results a theoretical basis for understanding the luminescent properties of these materials, complementing experimental studies and contributing to the broader understanding of phosphor behavior in WLED applications.

The group of materials studied in this chapter, $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ (SALON: Eu^{2+}), $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ (SLA: Eu^{2+}), $\text{Sr}[\text{Li}_3\text{AlO}_4]:\text{Eu}^{2+}$ (SLO: Eu^{2+}), and $\text{Ca}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ (CLA: Eu^{2+}), belongs to the UCr_4C_4 structural family. These materials have attracted attention over the last decade due to their potential in achieving narrow-band red emission, which is crucial for enhancing the color purity of WLEDs. Among these, the SALON: Eu^{2+} and SLA: Eu^{2+} phosphors were the subjects of two publications in 2021 [73] and 2023 [106], respectively. The sections of this chapter dedicated to these materials will closely follow these publications, and are more detailed than the other sections. In the case of SALON: Eu^{2+} , the IFCs embedding was not used at that time, meaning that the supercell sizes are not as large as in the others

materials and hence the results might not be as converged. Still, the physical interpretations from this study should remain valid.

5.1 $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$

Finding a highly efficient red emitting phosphor is crucial for a further increase in the luminous efficacy while keeping a high color-rendering index. In order to sufficiently cover the red spectral region while minimizing the efficacy loss caused by the eye poor long-wave sensitivity, red phosphors with narrow emission bandwidth showing a peak in the optimal red region are needed [15, 19].

In 2019, Hoerder et al. [32] reported the experimental discovery of a new narrow-band red-emission phosphor $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ (SALON) with an emission peak located at 614 nm, a FWHM of only 48 nm at room temperature and a low thermal quenching of 4% at operating temperature (420K). The fact that the emission peak is located at a shorter wavelength than its cousin $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ (SLA) [28] enables a gain of 16% in luminous efficacy compared to SLA, while keeping an excellent color rendering and thus enabling a potential leap in the energy efficiency of white-emitting phosphor-converted LEDs. SALON belongs to the UCr_4C_4 -structure family of phosphors, from which most interesting narrow-emission candidates have emerged recently [26, 27].

It was suggested by Hoerder et al. [32] that the narrow emission band of SALON originates from the Eu^{2+} optical center with high local-symmetry environment composed of a nearly cubic polyhedron of four oxygen and four nitrogen atoms, resulting in an isotropic structural relaxation upon emission. This would reduce the number of different energetic states involved in the emission process, leading to a narrow emission band [32]. Here, we show that this picture is incomplete.

In 2023, *after the publication* of the work on which this chapter is based [73], a combined theoretical and experimental work [105] demonstrated that, despite the expected eightfold coordination of Eu^{2+} ions by four N^{3-} and O^{2-} ions, X-ray diffraction could not definitively confirm the local coordination symmetry or the precise 1:1 ratio between the ligands. Alongside the dominant emission at 614 nm (with a 1:1 ratio), which exhibits vibronic fine structure at 10 K, weaker emission bands at 570 and 650 nm were identified. These were attributed to Eu^{2+} ions coordinated by N^{3-} and O^{2-} ions in a ratio differing from 1:1.

5.1.1 Structural properties

SALON crystallizes in a tetragonal phase (space group $P4_2/m$) with the unit-cell parameters $a = b = 7.959 \text{ \AA}$ and $c = 3.184 \text{ \AA}$ with 2 formula units (hence 18 atoms) per primitive cell. The structure is a variant of the

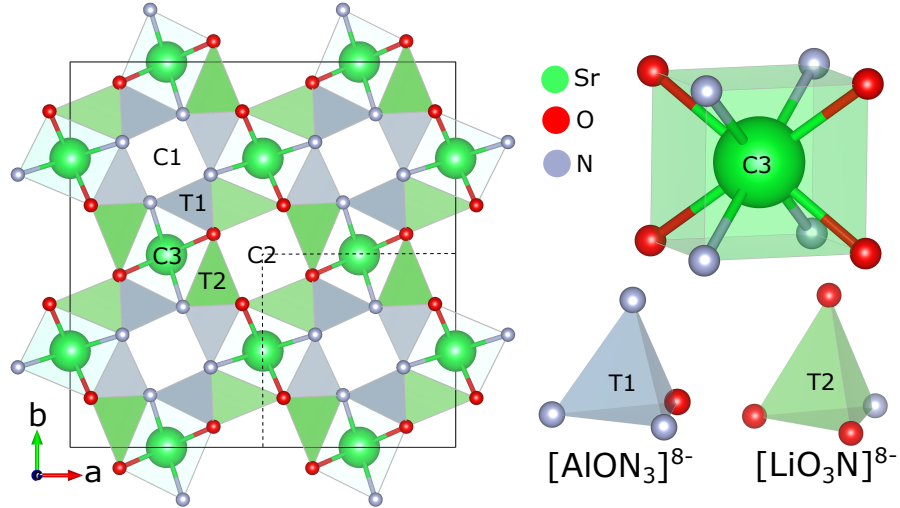


Figure 5.1: $2 \times 2 \times 2$ supercell of undoped SALON. Tetrahedra T1 are composed of aluminium coordinated with three nitrogen atoms and one oxygen atom forming a $[\text{AlON}_3]^{8-}$ unit. Tetrahedra T2 are composed of lithium coordinated with one nitrogen atom and three oxygen atoms forming a $[\text{LiO}_3\text{N}]^{8-}$ units. Three types of channels exist, of which two are empty (C1 and C2) and the third hosts strontium cations that are coordinated with four oxygen atoms and four nitrogen atoms in a nearly cubic environment. The unit cell is represented with dashed lines.

UCr_4C_4 structure type, well known in the field of phosphor materials to provide a highly condensed and rigid framework structure [26, 33, 34], with strontium on the corresponding uranium site, aluminium and lithium on the corresponding chromium site, and nitrogen and oxygen on the corresponding carbide site. Two tetrahedra types form a network hosting the strontium cations in one of the resulting channels shown in figure 5.1. Strontium atoms are coordinated with four nitrogen and four oxygen atoms which gives a highly-symmetrical cube-like coordination.

The structural parameters of undoped SALON computed within DFT are listed in Table 5.1. We observe globally a slight overestimation of the structural parameters by about 0.5-0.7 % which is common of GGA-PBE functionals. Since our computation neglects all vibrational

and anharmonic effects, while the experimental structure is measured at room-temperature, this error might be underestimated because of zero-point and thermal expansion effects. When a Sr atom is replaced by an Eu atom in the doped configuration, with a decrease of symmetry to point group $2/m$ (C_{2h}), we observe that the Eu-O and Eu-N bond lengths are quite close to the Sr-O and Sr-N bond lengths, which is reasonable since the experimental atomic radii of Eu and Sr in their VIII coordination state are very close; 1.39 and 1.40 Å, respectively [151]. In contrast, we also observe that the Eu-Sr length is more than 2 % bigger than the Sr-Sr length in the undoped structure.

	Exp. [32]	This work		
	Undoped	Undoped	Doped 4f	Doped 5d
a [Å]	7.959	8.013 (+0.67%)	8.012 (-0.01%)	8.012 (+0%)
b [Å]	7.959	8.013 (+0.67%)	8.012 (-0.01%)	8.012 (+0%)
c [Å]	38.208	38.438 (+0.60%)	38.442 (+0.01%)	38.442 (+0%)
X-Sr [Å]	3.184	3.131 (-1.66%)	3.206 (+2.39%)	3.171 (-1.10%)
X-O [Å]	2.659	2.667 (+0.30%)	2.678 (+0.41%)	2.633 (-1.71%)
X-N [Å]	2.760	2.782 (+0.79%)	2.784 (+0.07%)	2.738 (-1.68%)
O-X-O [°]	73.572	73.819 (+0.34%)	73.719 (-0.13%)	72.514 (-1.66%)
N-X-N [°]	70.446	70.301 (-0.21%)	70.356 (+0.08%)	70.628 (+0.39%)
Polyhedral volume [Å ³]	30.411	30.870 (+1.49%)	31.107 (+0.76%)	29.715 (-4.68%)

Table 5.1: Structural parameters of undoped and doped SALON, either in ground 4f or excited 5d state for a $1 \times 1 \times 12$ supercell. The X symbol refers to strontium when undoped and europium when doped. Polyhedral volume refers to the nearly cubic environment of Sr/Eu composed of 4 oxygen and 4 nitrogen atoms. The percentages in parentheses are calculated with respect to the previous column.

To understand the relaxation process accompanying the change in electronic density induced by the 5d-4f transition, a comparison is performed between the 4f-state geometry (A_g , A_g^*) and the 5d-state geometry (A_e^* , A_e), see figure 5.7. On the left and right of figure 5.7a, we present the highest occupied Kohn-Sham orbitals (norm of the wavefunctions) associated to the $4f^7(^8S_{7/2})$ ground and $4f^6(^7F_J)5d^1$ excited states. We can directly notice how the 5d orbital is much more spatially extended than the 4f orbital. In the middle of figure 5.7 (a), we

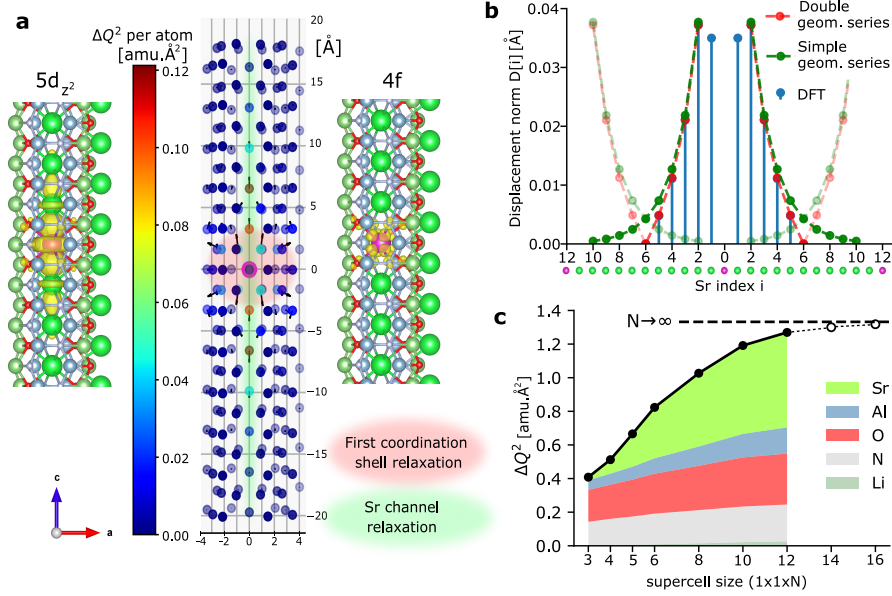


Figure 5.2: a) Excited state geometry and its highest $5d_{z^2}$ occupied orbital (left) compared to the ground state geometry and its highest $4f$ occupied orbital (right). The isosurface levels are the same. The atomic displacements induced by the electron density change is displayed in the middle of the figure. Central pink sphere represents Eu atom. The vector magnitude is multiplied by 25 for visualization. The color associated to each atom provides its contribution to the total normal coordinate change $(\Delta Q)^2$. Shaded areas indicates the two identified relaxation patterns. b) Blue points are DFT displacements induced by the $5d$ - $4f$ transition of the i -th distant Sr from Eu, projected on c -axis, in a $1 \times 1 \times 12$ supercell. The red curve is a sum of two counter-acting geometric series that models the effect of periodically arranged Eu. The green curve represents the displacements if Eu atom was completely isolated. Clear curves show the displacements associated to the first periodic replica. c) Convergence of $(\Delta Q)^2$ with the supercell size $1 \times 1 \times N$ with an atomic decomposition. Dashed black line represents the estimated converged value when $N \rightarrow \infty$. Empty circles estimate the values for larger supercells

present the displacement field associated to the $5d$ - $4f$ transition. The black vectors indicate the atomic displacements when going from the excited to the ground state ($\mathbf{R}_{e,\alpha} - \mathbf{R}_{g,\alpha}$) while the color associated to each atom provides its contribution to the total normal coordinate change $(\Delta Q_\alpha)^2 = \sum_i m_\alpha (R_{e;\alpha i} - R_{g;\alpha i})^2$. A more quantitative comparison between the ground and excited state environments is provided in Table 5.1.

From these results, we identify two important relaxation patterns when going from the 5d to 4f state. First, we observe a nearly isotropic expansion of the first coordination shell of Eu composed of four N and four O arranged in a nearly cubic environment (red-shaded area of figure 5.7 (a)), see the comparison between Eu-N length, Eu-O length, and polyhedral volume of excited and ground states. We justify the isotropic character of this expansion with the small O-Eu-O and N-Eu-N angle changes: no significant distortion effect is observed. In reference [98], the following explanation is given to this expansion effect: the bond length between an f-element ion in a $4f^N$ configuration and ligands is realized by the interaction between the $5p^6$ shell and the ligand's valence electrons. When the ion is in a $4f^{N-1}5d^1$ configuration, additional covalent interactions appear from the ligand to the inner 4f hole that shortens the bond length. We could also argue that the excited Eu^{2+} in the $4f^65d^1$ configuration gets closer to the Eu^{3+} configuration, leading to stronger Eu-O and Eu-N bonds, due to both Coulomb and covalent strengthening. This uncommon situation of a bond length shortening upon $f \rightarrow d$ excitation has been already observed experimentally and studied theoretically in various other lanthanide compounds [152–157].

Second, we observe a long-range relaxation of the strontium atoms belonging to the strontium channel containing the europium atom (see green shaded area of figure 5.7 (a)). When going from the 5d to 4f state, those strontium atoms are pushed away from europium along the c-axis. Comparing first the displacement magnitude of the two patterns, we observe that the displacements of the first distant Sr is slightly smaller than the O/N displacement associated to the first pattern. However, what matters in the luminescent properties is the normal coordinate change $(\Delta Q)^2$ (i.e., the displacement weighted by the atom masses), which explains why this second pattern is actually the dominant one, the Sr being heavier. It appears that about half of the total normal coordinate change comes from Sr displacements, see figure 5.7 (c).

It is surprising to observe that the displacement of the nearest Sr is slightly smaller than the second-nearest Sr. We attribute this effect to the large spatial extend of the $5d_{z^2}$ orbital. Beyond the second distant Sr, the Sr displacements follow an exponential decay, as explained later.

We performed a convergence study of $(\Delta Q)^2$ as a function of the supercell size. Increasing the number of atoms in the x-y plane ($\sqrt{2} \times \sqrt{2} \times N$ supercells) does not affect the result while increasing the Eu-Eu distance along c-axis does. Indeed, for too small $1 \times 1 \times N$ supercells, there

is a spurious cancellation of Sr displacements caused by periodically repeated Eu. The c-component of the supercell size (or equivalently the Eu-Eu distance) required to obtain a strictly converged $(\Delta Q)^2$ is very large, and instead, we model this cancellation effect by expressing the Sr displacements $D[i]$ in [Å] unit as a sum of two counter-acting decreasing geometric series,

$$D[i] = C(A^{(i-2)} - A^{(N_{Sr}-1-i)}), \quad (5.1)$$

where i labels the Sr atoms, N_{Sr} denotes the number of Sr atoms between two adjacent Eu, which is 11 in the case of the $1 \times 1 \times 12$ supercell used, and where C and A are the fitting coefficients. With $A = 0.58$ [/] and $C = 0.037$ [Å], the DFT displacements are well reproduced with this simple model, see red curve of figure 5.7 (b). In this figure, plain and transparent green curves refer respectively to the first and second terms of Equation 5.1. Note that we excluded the first Sr because of the above-mentioned reasons. If we now consider a perfectly isolated Eu, the Sr displacements would be expressed as a simple decreasing geometric series with the same fitting coefficients A and C (plain green curve). We compute the error made as the difference between the red and green displacements. In terms of normal coordinate change, this gives a difference of 0.028 [amu.²], a 4.8 % error with respect to the Sr contribution to the total $(\Delta Q)^2$. Indeed, these additional Sr displacements lead to small additional displacements of their atomic neighbors that we simply model with this same percentage error. In total, we estimate the strictly converged value (i.e., without finite supercell size effect) to be $(\Delta Q)^2 \approx 1.33$ [amu.²], 4.7 % higher than the computed DFT value. To our knowledge however, it is the first time that such long-range channel relaxation is theoretically highlighted and analyzed in phosphor materials. As it will be seen in sub-section 5.2.4, this greatly impacts the computed luminescent properties and it might be a common denominator that explains the particular luminescent properties of this type of phosphor materials.

5.1.2 Electronic properties

The electronic band structure and the partial density-of-states near the Fermi level of undoped SALON are presented in figure 5.3 (a), obtained with the relaxed cell parameters. The computed indirect band gap of undoped SALON is 3.44 eV, underestimating the experimental gap of 4.4 eV [32], a quite standard underestimation, often observed with

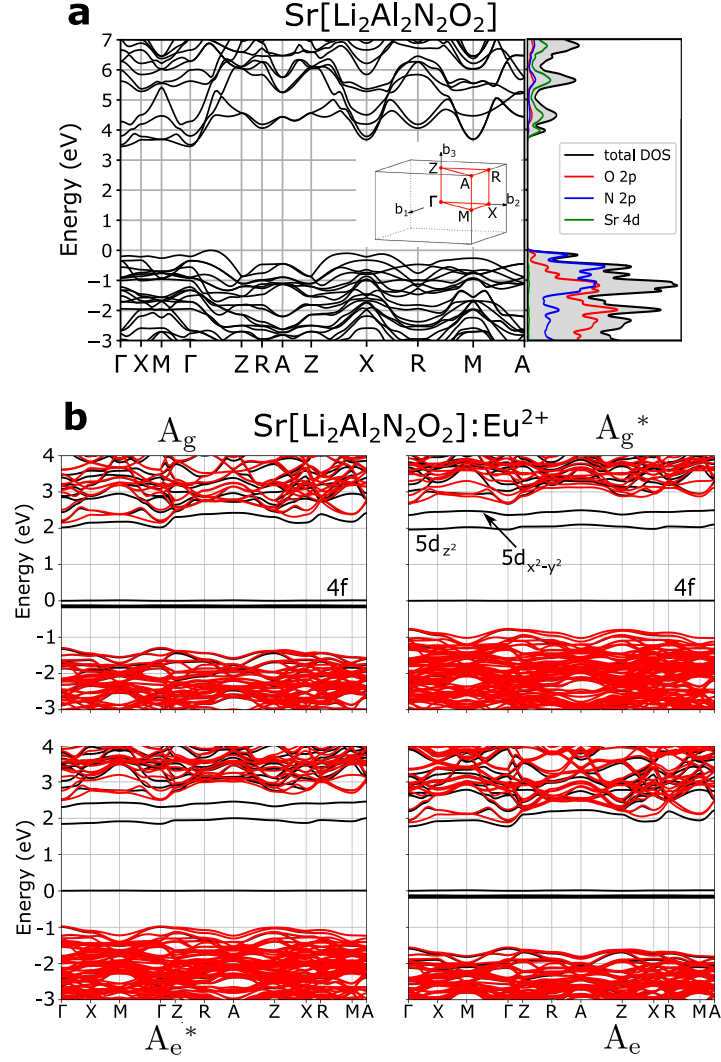


Figure 5.3: a) Electronic band structure of undoped SALON near the fermi level and the associated partial density of states. b) Electronic band structure of SALON:Eu. A_g , A_g^* , A_e^* , A_e refers to the notation used in chapter 3. Black and red curves distinguishes spin up from spin down electrons, respectively.

local or (semi-)local exchange-correlation functionals, like the presently used GGA-PBE. Figure 5.3 (b) shows the band structures of the four characteristic states of the one-dimensional coordinate model. In the gap, in addition to the 4f states, we observe one first 5d state, presenting mainly a $5d_{z^2}$ character, actually a superposition of $l = 2$, $m = -2, 0$ and 2 angular momentum components, belonging to the a_g irreducible

representation of the above-mentioned $2/m$ point group. It shows a small dispersion along the c -axis coming from a residual interaction between periodically repeated europium atoms. The next higher band lying in the band gap is identified as mainly $5d_{x^2-y^2}$. When in the excited state, the $4f$ -like hole state can also be analyzed in terms of its angular momentum components, showing a superposition of $l = 3$, $m = -3, -1, 1$ and 3 components, so belonging to the b_u irreducible representation of the above-mentioned $2/m$ point group.

5.1.3 Luminescent properties

E_{ZPL} (eV)	$E_{FC,g}$ (eV)	$E_{FC,e}$ (eV)	ΔS (eV)	
2.032	0.096	0.086	0.182	
ΔQ ($\sqrt{amu}$)	$\hbar\Omega_g$ (meV) / (cm^{-1})	$\hbar\Omega_e$ (meV) / (cm^{-1})	S_g	S_e
1.127	25.15 / 202.87	23.86 / 192.48	3.82	3.62

Table 5.2: 1D-CCM parameters of Eu-doped SALON computed with DFT.

We compute the luminescent properties of doped SALON and report the DFT parameters required for the 1D-CCM model in **Table 5.2**. We now present the results from the multi-phonon mode approach. The discrete partial Huang-Rhys factors S_ν are shown in Figure 5.4 (a) along with the spectral decomposition $S(\hbar\omega)$ (Gaussian smearing of 4 meV). The phonon density of states is displayed in the background of this figure.

This reveals the nature of the electron-phonon coupling associated to the $5d$ - $4f$ transition : At low energy (< 0.022 eV), phonon modes associated to Sr atoms dominates. This threshold is fixed such that, at 0.022 eV, Sr atoms contribute to half of the phonon density of states. It is also where a dip is observed in the spectral function. We highlight in this low-energy region the four modes presenting the highest partial Huang-Rhys factors S_ν . We present them in the phonon dispersion curve along Γ -Z in figure 5.4 (b) and we show their eigendisplacements in figure 5.4 (c) where the displacements have been scaled by a factor 10 for clarity. The mode that couples the most (i) is an acoustic mode directed along z , of high wavelength. On this same phonon branch,

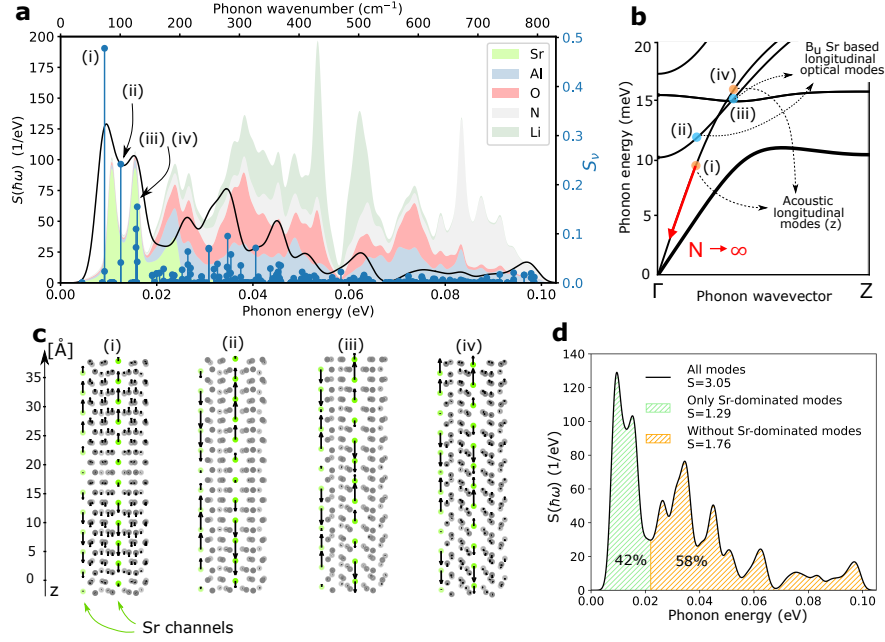


Figure 5.4: a) Partial Huang-Rhys factors S_v and spectral decomposition $S(\hbar\omega)$ using a 4 meV Gaussian broadening. The background shows the partial phonon density-of-states of undoped SALON. b) Phonon dispersion at low phonon energy between Γ -Z. High-coupling modes are highlighted. c) Visualization of the eigenvectors corresponding to the low-frequency high-coupling modes. d) Effect of Sr-dominated modes on the spectral decomposition.

the acoustic mode (iv) with half-wavelength also couples strongly. The mode (ii) presents a B_u representation where strontium atoms of different channels are out of phase. The mode (iii) corresponds to the same mode but with half-wavelength. Indeed, those long-wavelength collective displacements of the Sr atoms along the c-axis couple strongly with the above-described 5d-4f relaxation of the Sr channel containing Eu. It is noted that the experimental spectrum measured latter in 2023 [105] allowed to resolve some peaks in the PL spectrum. A spacing of 113 cm^{-1} (0.014 eV) was found between the ZPL line and the first phonon peak. This corresponds precisely to the predicted coupling with Sr-based phonon modes.

Above 0.022 eV , the spectral decomposition is made of a multitude of modes containing Al, O, and N displacements. We still notice the large peak around 0.035 eV composed of modes that couple strongly with the relaxation of the first coordination shell of Eu (expansion of the

nearly cubic environment of Eu). This coupling to a large number of modes instead of one single effective “breathing” mode coincides with the results of Linderälv *et al.* [92] where a similar feature was found with YAG:Ce³⁺ phosphor. In figure 5.4 (d), we quantify the importance of Sr-dominated phonon modes by computing their contribution to the total Huang-Rhys factor and found out that the Sr-dominated modes contributes 42% to the narrow emission in Sr[Li₂Al₂O₂N₂]:Eu²⁺.

For completeness, the convergence of this spectral decomposition as a function of the supercell size is presented in the appendix. It indicates that the result is well converged for high phonon energies while the exact shape of the low energy part of $S(\hbar\omega)$, composed of modes involving Sr atoms, is not yet totally converged. By increasing the supercell size further, one would simply displace the points highlighted in figure 5.4 (b) towards Γ on their corresponding branches. This concern reflects first the difficulty to obtain a strict convergence of the structural relaxation of the Sr channel, as described in section 5.1.1. Second, due to the coupling to high-wavelength acoustic phonon modes, obtaining a strict convergence of the low-energy shape requires also to obtain a denser sampling of those phonons. Embedding methods to increase the supercell size can be used to tackle this problem [58, 117]. This improvement, latter implemented during the PhD thesis, will be shown in the following sections of this manuscript.

The total Huang-Rhys factor $S_{\text{multi-D}} = \sum_{\nu} S_{\nu}$ is 3.05, smaller than the one-dimensional $S_{1D} = 3.82$. One shows, with the same $E_{\text{FC,g}}$ definition, that $S_{1D} \propto (\sum_{\nu} p_{\nu} \omega_{\nu}^2)^{1/2}$ is always larger than $S_{\text{multi-D}} = \sum_{\nu} S_{\nu} \propto \sum_{\nu} p_{\nu} \omega_{\nu}$. S_{1D} deviates largely from $S_{\text{multi-D}}$ when the spread of the spectral function $S(\hbar\omega)$ is large, which is the case here. Following the generating function approach described in chapter 3, the emission spectral function $A(\hbar\omega)$ was calculated based on the spectral decomposition $S(\hbar\omega)$. The resulting curve is then convoluted with a Gaussian of fixed width. The normalized luminescence intensity is finally obtained by considering the cubic frequency dependence : $L(\hbar\omega) = C\omega^3 A(\hbar\omega)$.

In the appendix, we present the luminescence intensity as computed in this work at 0 K following the 1D model, the multi-D model without the Sr-dominated modes (only considering the orange area of figure 5.4 (d)) and the full multi-D model with all modes. No shift of the zero-phonon line was considered and a small smearing was applied.

In order to compare these results with the experimental spectrum (15K) and to deal with the indeterminacy of the experimental E_{ZPL} , we proceed in the following way. For each case, we adjust the shift of the

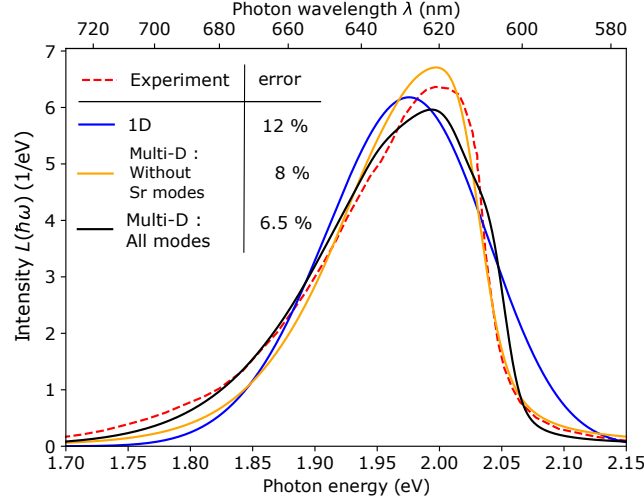


Figure 5.5: Comparison of normalized luminescence intensity $L(\hbar\omega)$ with experiment. Blue: 1D model, with a single effective mode. Orange: multi-dimensional model, where the Sr-dominated modes were excluded. Black: multi-dimensional model, with a full phonon decomposition. For each curve, the broadening parameters and E_{ZPL} were optimized to minimize the error as defined in the text. The best fit is obtained within the multi-dimensional model when all phonon modes are taken into account.

curve (modification of E_{ZPL}) and the broadening parameters to minimize the error defined as the integral of the absolute difference between the simulated and experimental curves (in energy scale), divided by two. Since all spectra are normalized such that $\int L(\hbar\omega)d(\hbar\omega) = 1$, this ensures an error bounded to $[0 - 1]$. The resulting curves are presented in figure 5.5.

We find that, in the 1D case, the best fit gives an error of 12 %. In the multi-D case without considering the Sr-dominated modes, an error of 8 % is found. Using all the phonon modes in the multi-D model gives the best fit (error of 6.5 %).

The broadening parameters used refer physically to homogeneous and inhomogeneous broadening are used as fitting parameters to match the experimental emission spectrum shape and no physical conclusion should be drawn from the values that give the best fit.

We note first that the 1D model does not reproduce well the shape of the experimental spectrum. Indeed, it has been shown that the single mode approximation is well justified for a large coupling $S \gg 1$, which is not the case here. We have also seen that S_{1D} overestimates the more

precise $S_{\text{multi-D}}$. Moreover, the spectral decomposition $S(\hbar\omega)$ is highly asymmetric around the effective frequency : an important weight on a short energy range at low energy and relatively broad distribution after 25-30 meV. This fine feature cannot be captured well by assuming only one effective mode as done in the 1D model. We observe also that considering all the phonon modes, including the Sr-dominated ones, allows to obtain the best match with the experiment. In particular, the long tail of the spectrum is only well reproduced with the full computation. This underlies the importance of the long-range Sr displacements in shaping the emission spectrum of $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$. Surprisingly, the spectrum obtained without those Sr modes provides already a good estimate of the experiment. This is however fortuitous : indeed, by only considering the high-energy part of $S(\hbar\omega)$, the total Huang-Rhys factor is decreased but the effective frequency is increased. On the emission spectrum, these two effects are counter balancing each other, which explains the small difference between orange and black curve of figure 5.5.

To conclude this section, we make the link between the small FWHM of the emission spectrum of SALON with its particular structure. A small FWHM is achieved by reducing at the same time the normal coordinate change ΔQ and the effective frequency $\hbar\Omega_g$ (see Equation (1.7)). In the case of SALON, the small ΔQ comes from the high rigidity of the host structure. The small effective frequency, on the other hand, comes from the large coupling of the Sr channel relaxation with low-frequency phonon modes involving these channels. In 2021, we believed that those features were not specific to SALON but were also valid for other UCr_4C_4 type phosphors that present a rigid host structure and this peculiar Ca/Sr/Ba channel. We will show in the next sections that this hypothesis is true.

5.2 $\text{Sr}[\text{LiAl}_3\text{N}_4]: \text{Eu}^{2+}$

Despite the pioneer status and technological relevance of $\text{Sr}[\text{LiAl}_3\text{N}_4]: \text{Eu}^{2+}$ (SLA) [158], its phonon side bands with apparent vibronic signatures have not received any theoretical attention until now. Initial theoretical studies of SLA focused on the bulk host material only [159, 160]. Recently, a time-dependent DFT approach for embedded clusters has clarified the electronic processes responsible for light absorption in SLA but has not investigated emission and the PL spectrum [102]. In SLA, the europium dopant can substitute the strontium atom in two inequivalent positions, which lead to two emission centers. Thanks to their different decay time, time-resolved luminescence was used in 2016 to decompose the zero-phonon line (ZPLs), 15377 cm^{-1} (1.906 eV) and 15780 cm^{-1} (1.956 eV), and corresponding phonon side bands of each center but their structural assignment was not done [161].

In this work, we study from first-principles the vibronic processes occurring in the PL spectrum of $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ (SLA) phosphor. We simulate the PL spectra from the two luminescent sites and assign them to their specific microscopic environment.

We use large supercells computed with density functional theory (DFT) and the constrained- ΔSCF method to obtain optimized Eu-4f ground state structures and Eu-5d excited state structures. The atomic displacements induced by the 5d-4f transitions are projected onto the phonons modes of the system in order to obtain the Huang-Rhys (HR) spectral function which provides information on the nature of the phonons participating to the transition. The HR spectral function is converged by increasing the supercell size using the embedding procedure proposed by Alkauskas *et al.* [58]. The PL lineshape is computed following the generating function approach and its temperature-dependent generalization [59]. Finally, the effect of thermal expansion on PL properties is included via the volumic quasi-harmonic approximation (QHA) [162, 163] with a minimization of the Helmholtz free energy with respect to the global volume. This allows one to estimate ZPL energies with increasing temperatures.

5.2.1 *Ground state geometry*

The SLA crystallizes in a triclinic crystal system ($P\bar{1}$ space group) with the typical channel structure observed in other UCr_4C_4 type phosphors, see figure 5.6. Our computed lattice parameters are overestimated

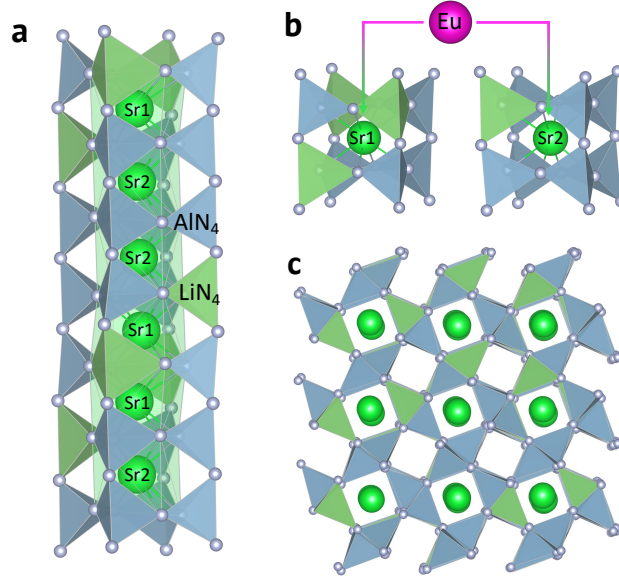


Figure 5.6: **a** Crystal structure of $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ viewed along the Sr chain. **b** First- and second-shell environments of Sr1 and Sr2 sites that Eu atom can substitute. **c** Structure perpendicular to the Sr chains, with the characteristic UCr_4C_4 framework.

by about 0.3%, which is common for PBE exchange and correlation functionals. The angles match within 0.05° difference. Half of the channels are occupied by the Sr^{2+} ions. These channels are built up with ordered tetrahedra alignment as seen in figure 5.6 (a), with one green $[\text{LiN}_4]^{11-}$ followed by three blue $[\text{AlN}_4]^{9-}$. Two Sr sites with very similar first-shell environment (Sr-N_8) but different second-shell can host the Eu activator and are shown in figure 5.6 (b), which leads to two emission centers. The first site, denoted as Sr1 in this work, is surrounded by 3 $[\text{LiN}_4]^{11-}$ and 5 $[\text{AlN}_4]^{9-}$ tetrahedra, while the second, denoted as Sr2, is surrounded by one $[\text{LiN}_4]^{11-}$ and 7 $[\text{AlN}_4]^{9-}$ tetrahedra. We observe that within the Sr chain, the Sr1-Sr1 distance of 3.2 Å is shorter than the Sr2-Sr2 distance of 3.42 Å. The Sr1-Sr2 distance is in between with a value of 3.28 Å. We compute that the Sr-N_8 cuboid has similar mean Sr-N distance in both sites (2.809 Å and 2.804 Å) When the Sr atoms are replaced by Eu atoms, these distances change by less than 0.1% due to similar atomic radii for the Eu^{2+} and Sr^{2+} atoms [151].

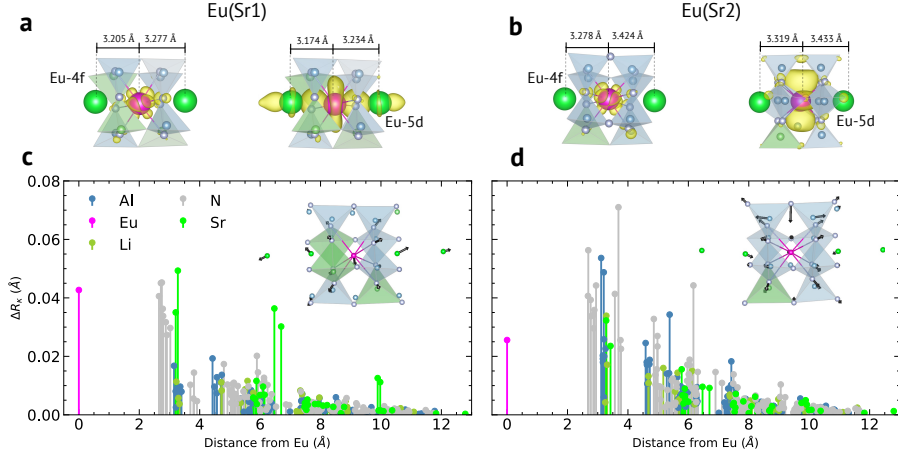


Figure 5.7: The probability density of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8S_{7/2})$ ground and lowest $4f^6(^7F_1)5d^1$ excited states, for **a** Eu(Sr1) site and **b** Eu(Sr2) site. Norm of the atomic displacements induced by the 5d to 4f transition (upon emission) for **c** Eu(Sr1) site and **d** Eu(Sr2) site as a function of the distance from Eu. The insets show a three-dimensional view of these displacements near the Eu activator, scaled by 20 for clarity.

5.2.2 Excited state geometry

The probability density of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8S_{7/2})$ ground and lowest $4f^6(^7F_1)5d^1$ excited states are presented in figure 5.7 (a)-(b) for both Sr sites. The computed energy levels are reported in the appendix, on figure A.7. In a hypothetical pure cubic EuN_8 environment, $5d_{z^2}$ and $5d_{x^2-y^2}$ would be the lowest degenerate d-states. However, this degeneracy is lifted when considering a non-perfect EuN_8 cuboid with different second shell environment ($[\text{LiN}_4]^{11-}$ and $[\text{AlN}_4]^{9-}$ tetrahedra) and different Eu-Sr distances along the 1D Sr chain.

In the case of Eu(Sr1), we observe that a $5d_{z^2}$ -like orbital is stabilized along the Sr chain as in the case of $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ [73]. The $5d_{x^2-y^2}$ -like state is also located in the band gap, but 0.27 eV above the $5d_{z^2}$ -like state.

In contrast, for Eu(Sr2), the opposite situation appears: a $5d_{x^2-y^2}$ -like orbital is stabilized, perpendicular to the Sr chain. The four lobes point toward the interstitial area of low electrostatic potential produced by nitrogen ligands. The inversion of the 5d states ordering appears

to be related to the difference in second-shell environments, given the similarity of the Eu-N₈ cuboids. However, it is unclear whether the inversion is caused by the difference in Eu-Sr distances (steric effect) or the difference in tetrahedra types (coulombic effect). To explore this further, we have relaxed a fictitious system in which the Eu atom replaces Sr₁, while keeping the Eu-Sr distances fixed at the relaxed Eu(Sr₂) values. Our findings indicate that the 5d_{z²} state remains stabilized, but the 5d_{x²-y²} state is now 0.15 eV above. This suggests that the difference in tetrahedra types is the primary explanation for the inversion of the 5d states, with some contribution from the difference in Eu-Sr distances.

We stress that in reference [102], it was argued that the similar local geometry and electronic structure between the two sites leads to a similar emission spectrum. However, our computations contradict this claim. Indeed, we have found that the two sites possess different electronic structures that result in distinct emission spectra, as it will be demonstrated later on. We also find that for both sites, the computed energy separation between the empty 5d state and the conduction bottom (Sr-4d character) is 0.29 eV. Experimentally, the 5d-conduction band separation is estimated to be 0.28 eV [160] based on a fitting of thermal quenching data with an exponential non-radiative decay rate from the 5d state to the conduction bottom through thermal excitation. Despite the good agreement between these values, it is important to remember that the Kohn-Sham energy levels calculated using GGA-PBE are only approximations of the actual energy levels and this agreement should be appreciated with caution.

The displacement field associated to the 5d-4f transition is presented in the insets of figure 5.7 (c)-(d), scaled by 20 for clarity. The norm of these displacements is shown as a function of the distance from the Eu activator. For both Sr sites, upon emission, going from the 5d to 4f state leads to an elongation of Eu-N bond lengths by 0.03-0.06 Å. Indeed, upon 5d excitation, additional covalent interactions appear between the N ligands with the inner 4f hole that shortens the bond length [98]. Interestingly, the Eu atom moves in its cuboid cage as a result of its non-symmetrical environment. Looking now at the atomic rearrangements beyond the first coordination shell, we see first that a significant fraction of the total displacements is outside this first shell, as observed in similar UC₄C₄ phosphors [38, 73]. This fact might be linked to the rigid structure (we compute a Debye temperature of 878.5 K) that distributes the local strain caused by the localized 5d-4f

excitation to atoms far away from the Eu activator. Quantitatively, 61% of the total mass-weighted displacements $\Delta Q = \sqrt{\sum_k M_k \Delta R_k^2}$ is contained in the Eu-N₈ cuboid for Eu(Sr1) and 50% for Eu(Sr2). Given its mass, the Eu atom contributes to this ΔQ up to 49% in Eu(Sr1) and to 30% in Eu(Sr2).

By inspecting closely the difference between Eu(Sr1) and Eu(Sr2), we observe that the main relaxation pattern in Eu(Sr1) is a long-range displacement of the Sr chain, as already observed in Sr[Li₂Al₂O₂N₂]:Eu²⁺, which is a consequence of the 5d_{z²} orientation along this chain. Given the high Sr mass, we expect that the Sr displacements are predominant in shaping the electron-phonon spectral function of Eu(Sr1), as will be seen later. For Eu(Sr2), a major fraction of the displacements are distributed on the adjacent [LiN₄]¹¹⁻ and [AlN₄]⁹⁻ tetrahedra, which is a consequence of the 5d_{x²-y²} lobes pointing towards it. We provide the structural parameters for pristine SLA, doped SLA Eu(Sr1) and Eu(Sr2) in their 4f and 5d states in the appendix A. Finally, the energy between the computed relaxed excited and ground states provides an estimation of the ZPL energies, $E_{\text{ZPL-Sr1}}=1.916$ eV and $E_{\text{ZPL-Sr2}}= 1.989$ eV, close to the experimental ZPL energies of 1.906 eV and 1.956 eV, respectively. While the agreement is remarkable, it should be taken with caution, as the computational method itself does not inherently guarantee an accuracy of a few meV, and the close match may result from error compensation. In order to explain this difference in ZPL energies, one might invoke the difference in [EuN₈] cuboid volumes between the two sites, as it was done in reference [26] to explain the variation of emission energies across different oxy-nitrides and alkali-lithosilicates. However, the very small difference between the two cuboids volumes ($\approx 1\%$) is not sufficient to explain the difference in ZPL energies. We believe that the different degree of ionicity experienced by the 5d orbital due to the different number of [LiN₄]¹¹⁻ and [AlN₄]⁹⁻ tetrahedra is responsible for the difference in ZPL energies. As a rough estimate, Eu(Sr1) with 3[LiN₄]¹¹⁻ and 5[AlN₄]⁹⁻ has a second-shell formal charge of -78 e while Eu(Sr2) with 1[LiN₄]¹¹⁻ and 7[AlN₄]⁹⁻ has a second-shell formal charge of -74 e, where e is the absolute value of the electron charge. In SALON, this second shell formal charge is -64 e. This is in line with the experimental ZPL energies of 1.906 eV, 1.956 eV and 2.03 eV [105], respectively.

5.2.3 Huang-Rhys spectral function

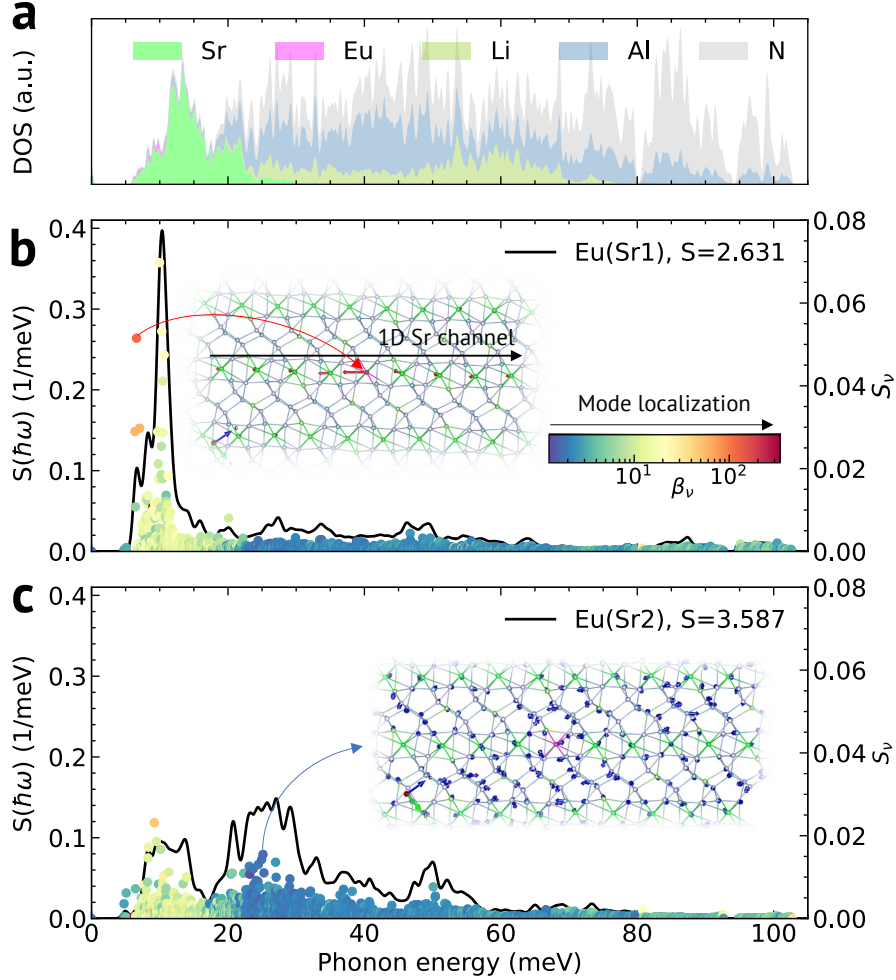


Figure 5.8: Spectral decomposition of the Huang-Rhys function obtained from the S_v (colored dots), $S(\hbar\omega) = \sum_v S_v \delta(\hbar\omega - \hbar\omega_v)$ (black lines), using a 1 meV Gaussian broadening, for both sites. In **a** we show the atom-projected phonon density-of-states. The height of the dots in **b** -for Eu(Sr1)- and **c** -for Eu(Sr2)- provides the partial Huang-Rhys factor of each phonon mode, while the color indicates the degree of localization of each mode β_v , see text. For each Sr site, two illustrative modes with high Huang-Rhys factor but different degree of localization are shown.

The Huang-Rhys spectral decomposition is presented in figure 5.8. A supercell containing 2304 atoms ($4 \times 4 \times 4$ supercell) is used thanks to the embedding procedure, described in the chapter 3, which allows

us to approach the dilute limit while keeping local and quasi-local modes brought by the Eu defect. The localization of the phonon modes can be characterized by computing the inverse participation ratio (IPR) and the localization ratio β_v as defined in references [38, 58, 59]. We show in figure 5.8b-c the color-coded mode localization β_v , which combined with the atom-projected phonon density of states in figure 5.8a, shows that the low-energy modes are more localized and dominate the electron-phonon coupling associated with the 5d-4f transition in the case of Eu(Sr1).

For Eu(Sr1), the spectral function is dominated by a large peak around 10 meV where low-frequency phonon modes associated to Sr and Eu displacements are involved. They mostly correspond to long-wavelength collective displacements of the Sr atoms along the Sr chain that couple strongly with the above-described 5d-4f relaxation of the Sr channel containing Eu. We compute a total Huang-Rhys factor $S = \sum_v S_v$ of 2.631 in that case and find that the phonons with high partial HR factor S_v can be either relatively delocalized or very localized. For instance, the highest coupling mode at 9.97 meV with $S_v=0.07$ has a β_v of 23. This mode is associated to the collective displacements of all the Sr atoms in the chain and can be considered as a slightly perturbed bulk mode. In contrast, the third highest coupling mode at 6.6 meV is very localized, with a $S_v=0.05$ and a large β_v of 115. As illustrated in the inset of figure 5.8b, the atomic vibrations associated with this mode (red arrows) are localized around the Eu doping atom.

In the case of the second site Eu(Sr2), the spectral function indicates that the phonon modes involving Eu and Sr atoms participate but to a lesser extent than in the Eu(Sr1) case. Additionally, a broad peak appears between 20 meV and 40 meV which is associated to modes involving Al and N atoms. The total Huang-Rhys factor of 3.587 indicates a stronger electron-phonon coupling. The highest coupling mode located at 9.2 meV with $S_v=0.023$ has a β_v of 59. This mode is mostly associated with the Eu atom moving in its cage. Similarly to the Eu(Sr1) case, there is also a number of delocalized bulk modes that contribute. Indicatively, the fifth highest coupling mode at 25.1 meV, with a $S_v=0.015$ has a β_v of 1.7 and is illustrated in the inset of figure 5.8c. The atomic vibrations associated to this mode (blue arrows) are distributed mainly on Al and N atoms in the whole system.

5.2.4 Photoluminescence spectrum and its temperature dependence

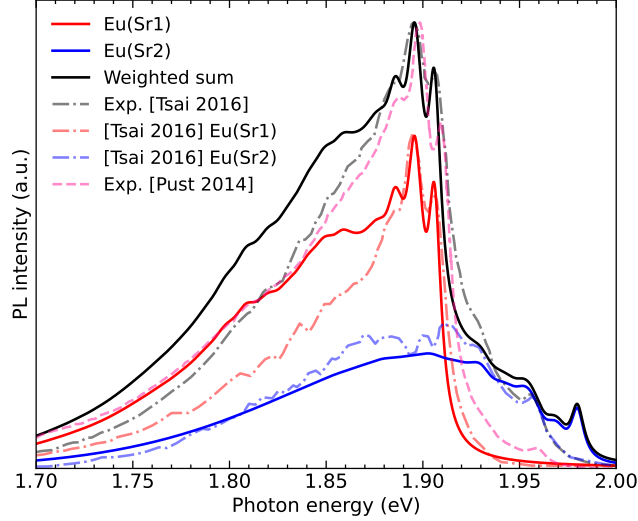


Figure 5.9: Computed photoluminescence intensities $L(\hbar\omega)$ for both Sr sites at 0 K and their weighted sum compared with two low-temperature experiments [28, 161]. The red and blue dotted curves are the experimental PL intensities of both sites from reference [161], where the total PL intensity (gray dotted curve) was deconvoluted with time-resolved spectroscopy. The computed Eu(Sr1) zero-phonon line energy is aligned with the second highest peak of the experimental data from reference [161] and the two weights for the black line are also taken from reference [161]. Reproduced with permission from references [28, 161]. Copyright 2014 Springer Nature and Copyright 2016 John Wiley and Sons.

We compute the photoluminescence (PL) intensity from the Huang-Rhys spectral function. Figure 5.9 compares the PL spectra from both sites at zero temperature with the experimental PL intensities at 10 K from reference [161], where the total PL intensity was deconvoluted with time-resolved spectroscopy (red and blue dotted curves). The total spectrum is also in good agreement with prior measurements at 6 K [28].

For definitiveness, we have (i) aligned our computed ZPL energy of Eu(Sr1) with the highest experimental peak [161], (ii) used a constant Lorentzian broadening of 25 meV, and (iii) used the experimental Eu(Sr1) to Eu(Sr2) total intensity ratio (computed as the ratio between the areas under the curves) from reference [161]. We do not attempt in this work to compute these weights from first principles, which would

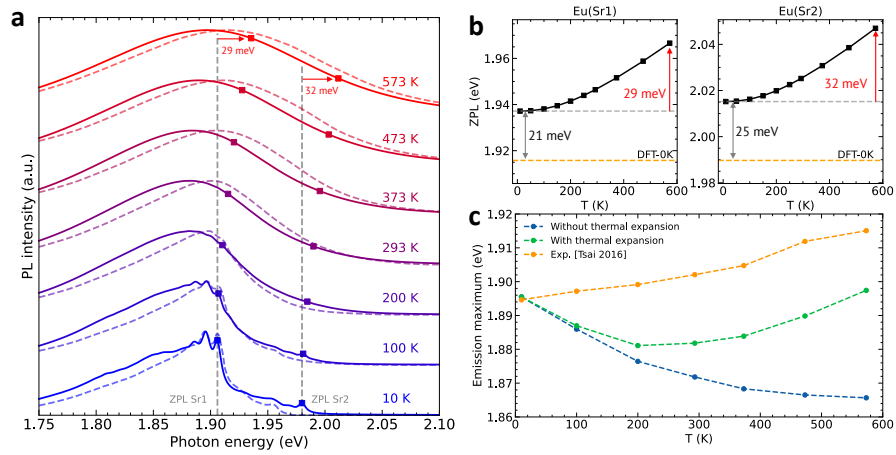


Figure 5.10: **a** Computed temperature-dependent photoluminescence (PL) spectrum (plain curves) compared with experimental data [161] (dashed curves). The zero-phonon line (ZPL) energies at 0 K are indicated by gray vertical dashed lines and the ZPL including thermal expansion effects are indicated with squares. The PL spectra for each temperature is shifted vertically for clarity. **b** Effect of thermal expansion on the ZPL energies for both sites where the DFT values at 0 K are shown with horizontal orange dashed lines. The shift associated with the zero-point volume are 21 and 25 meV, respectively. Between 0 K and 573 K, thermal expansion leads to a blue shift of 29 meV and 32 meV, respectively. **c** Photon energy of the emission maximum as a function of temperature. Ignoring thermal expansion leads to a red shift of the emission maximum. Adding the thermal expansion effect allows to obtain a better agreement with the experiment.

require to compare correctly the energetics and the electric dipole matrix elements of both sites. Indeed, the weight of the second PL intensity (ZPL at 1.956 eV) is different between the two experiments, which could be explained by different synthesis conditions. We note also that the energy difference between the experimental ZPL energies is 50 meV while the computed energy difference is 74 meV. This explains the misalignment observed in figure 5.9 between the experimental Eu(Sr2) ZPL and the computed one.

The vibronic peaks appearing in the experimental spectra as well as the global shapes of both spectra match our computations which means that the sharper PL spectrum with ZPL at 1.906 eV can be assigned with confidence to the Sr1 site while the broader spectrum with ZPL at 1.956 eV is assigned to the Sr2 site. When looking at the total experimental spectrum, the high-energy peak at 1.956 eV can be assigned to the ZPL of Eu(Sr2) center, the peak at 1.906 eV to the ZPL of Eu(Sr1) center, and the two next peaks to the one- and two-phonon contributions of strontium based phonon modes in Eu(Sr1). We still note that our computed total Huang-Rhys factor for Eu(Sr1) S_1 seems slightly overestimated. In order to estimate the experimental S_1 , the 5d-4f forces can be scaled in order to fit the experimental spectrum. Scaling the forces by 90% (giving $S_1^{\text{exp}} \approx 2.13$) allows one to obtain an excellent reproduction of the experimental phonon side-band (see figure A.9 in the appendix).

Finally, all the elements can be placed together to compute the temperature-dependent PL spectrum of SLA using the equations of section 2.3 which we present in figure 5.10 (a).

The effect of thermal expansion on the ZPL energy is quite similar for both sites and leads to a blue-shift of 29 and 32 meV from 0 to 573K, see figure 5.10 (b). The ZPL shifts associated to the zero-point volume are estimated to be 21 and 25 meV. Additional informations on thermal expansion calculations can be found in the appendix, section A.3. With increasing temperature, the spectrum broadens, with a progressive loss of clear vibronic peaks.

Figure 5.10 (c) presents the position of the emission maximum as a function of temperature, both with and without accounting for thermal expansion. When thermal expansion is not considered, a red-shift between 10 K and 573 K is computed. This is attributed to the positioning of the vibronic transitions that are activated by temperature relative to the emission maximum. Above 200K, where the position of the emission maximum is determined by the envelope of the vibronic trans-

itions, accounting for thermal expansion yields the temperature dependence observed experimentally. We notice that the ω^3 dependence of $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$ causes a blue shift of the emission maximum due to the broadening of the lineshape function $A(\hbar\omega)$ with temperature, even if $A(\hbar\omega)$ does not shift. This leads to a blue shift of +11 meV between 0K and 573K (see appendix, section A.3). Our analysis sheds new light on the puzzling phenomenon of temperature-induced shift in phosphor materials, which remains theoretically underexplored [164, 165]. It highlights the importance of both the ω^3 dependence of the PL intensity and the effect of thermal expansion.

5.3 $\text{Sr}[\text{Li}_3\text{AlO}_4]: \text{Eu}^{2+}$

Phosphors that emit in the green and yellow spectral regions are particularly important for achieving high luminous efficacy and optimal color rendering in pc-LEDs. In this context, oxo(nitrido)lithoaluminates, including well-known materials such as $\text{Ca}[\text{LiAl}_3\text{N}_4]$ and $\text{Sr}[\text{LiAl}_3\text{N}_4]$, demonstrate excellent red-emitting properties when activated by Eu^{2+} . Recently, the compound $\text{Sr}[\text{Li}_3\text{AlO}_4]$ (nicknamed SLO) was synthesized [39]. When doped with Eu^{2+} , it presents yellow luminescence, broadening the scope of narrow-band phosphors for solid-state lighting. The material was also independently reported in two patents [166, 167] and briefly mentioned in reference [168].

$\text{Sr}[\text{Li}_3\text{AlO}_4]$ adopts an ordered structural variant of the $\text{U}[\text{Cr}_4\text{C}_4]$ structure type, showing interesting quasi one-dimensional Sr chains. It is structurally very close to $\text{Sr}[\text{LiAl}_3\text{N}_4]$, already studied in this thesis.

Two Sr crystallographic sites are available for Eu^{2+} doping. The change lies in the second-coordination spheres, consisting of one Al and seven Li atoms (Sr1 site), and three Al and five Li atoms (Sr2 site). In $\text{SrLiAl}_3\text{N}_4$, the second shell of the two Sr sites are composed of five Al and three Li atoms, and seven Al and one Li atom.

The emission spectrum peaks at 572nm and has a FWHM of 47 nm. The shift of spectral position of the emission band to higher energies can be explained by the reduced nephelauxetic effect regarding oxygen ligands compared to nitrogen ligands in the first coordination sphere. In the crystal structure of $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ (emission maximum at 654nm), only Eu-N bonds are present and the covalency reduces for the Eu-N/O bonds in $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ (614nm) to exclusively Eu-O bonds in $\text{Sr}[\text{Li}_3\text{AlO}_4]: \text{Eu}^{2+}$ (572nm).

Like most other UCr_4C_4 phosphors, $\text{SrLi}_3\text{AlO}_4: \text{Eu}^{2+}$ shows good thermal quenching resistance. It retains over 93% of its photoluminescence intensity at 423 K compared to its room temperature performance. This makes it an attractive candidate for high-power pc-LED applications.

To further investigate the luminescent properties, ΔSCF calculations have been performed on this material. Figure 5.11 presents for each site, the probability density associated to the highest occupied Kohn-Sham levels. In both cases, the ground Eu_{4f} -like state are very localized on the Eu site. Interestingly, and in contrast to the SLA case, a $\text{Eu}_{5d_{2-2}}$ state is stabilized in the excited state for each site. The atomic relaxation show hence similar patterns ; a Eu- O_8 cuboid contraction (when going

from 4f to 5d), accompanied by a long-range channel Sr displacements. As in the case of $\text{SrLiAl}_3\text{N}_4$, the fact that the first-shell cuboid is not perfectly symmetric leads to a net displacement of the Eu atom. This also means that the Sr atoms are not moving perfectly aligned to the Sr channel. The magnitude of these displacements are shown on figure 5.11 as a function of the distance from the Eu dopant. The forces exerted on the atoms in the unrelaxed ground state are also presented. The table 5.4 decomposes the total normal coordinate change ΔQ^2 of each site into the different species present in the structure, and allows a quick comparison with the other UCr_4C_4 phosphors studied in this work. The discussion on this decomposition can be found in the section 6.5.

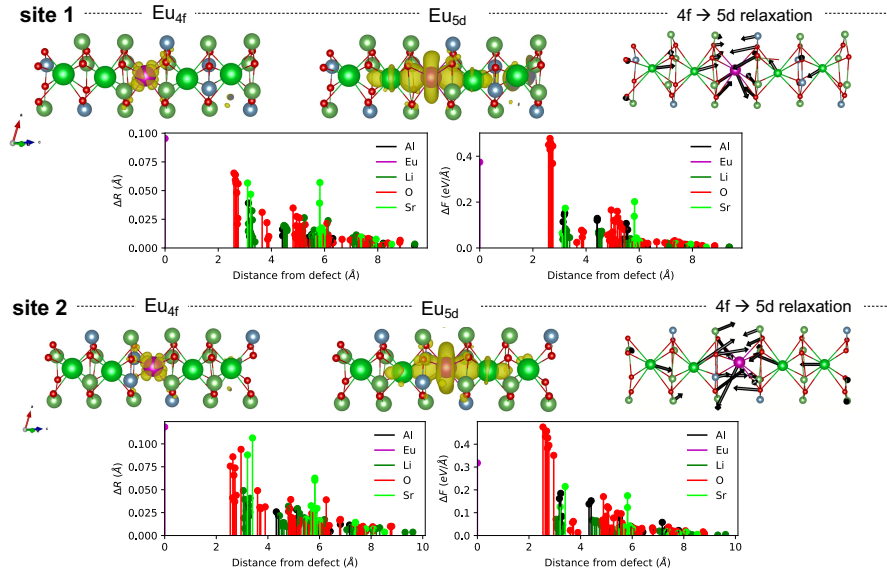


Figure 5.11: The probability density of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8S_{7/2})$ ground and lowest $4f^6(^7F_J)5d^1$ excited states, for Eu(Sr1) site and Eu(Sr2) site in $\text{SrLi}_3\text{AlO}_4: \text{Eu}^{2+}$. On the right, a three-dimensional view of the displacements near the Eu activator accompanying the electronic transition, scaled by 20 for clarity. On the bottom, the norm of the atomic displacements ΔR and forces ΔF induced by the 5d to 4f transition site as a function of the distance from Eu.

The computed parameters entering the 1D-CCM can be found in the table 5.2. We compute rather large Huang-Rhys factors compared to other $\text{U}[\text{Cr}_4\text{C}_4]$ phosphors. The emission energies are respectively 2.145 and 2.309 eV. With an experimental emission peak at 2.167 eV,

this suggest that most of the intensity originates from Eu atom doping Sr1 site. For the site 1, $S \approx 6.6$ and for the site 2, $S \approx 10.4$, meaning that we approach the strong coupling regime leading to gaussian-shaped spectra. In such a case, the 1D effective phonon mode model is sufficient, as explained in chapter 2. Figure 5.12 displays the theoretical single effective phonon spectra of site 1 and 2 versus the experiment at 300K. There is a good agreement between the Eu(Sr1) site spectrum and the experiment. Moreover, one can distinguish a small bump at around 2.4 eV in the experimental curve, which might be the signature of a small contribution of the Eu(Sr2) spectrum. The computed peak location of the PL spectrum of Eu(Sr2) support this hypothesis. We also note that the "bump" is larger for stronger Eu concentration, as reported in the patent [166].

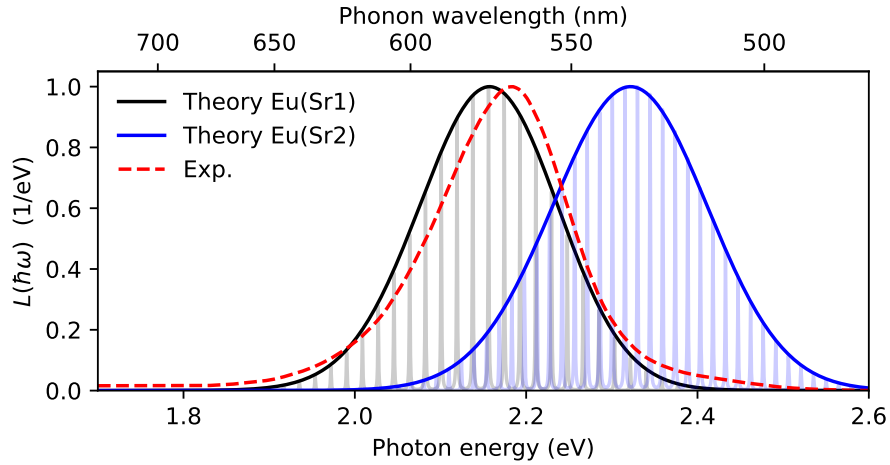


Figure 5.12: Experimental ($T=300\text{K}$) [39] and theoretical PL spectrum of $\text{Sr}[\text{Li}_3\text{AlO}_4]:\text{Eu}^{2+}$, as computed in this work following an effective phonon mode model.

It is interesting to note that, despite a much larger Huang Rhys factor, the Eu(Sr2) PL spectrum is not much broader ($\text{FWHM}_{\text{Sr1}} \approx 0.191 \text{ eV}$, $\text{FWHM}_{\text{Sr2}} \approx 0.217 \text{ eV}$). This is because the effective frequency of site 2 (14.67 meV) is smaller than the one of site 1 (18.40 meV). In both cases, the effective frequency is small because of the coupling with heavy Sr-based phonon modes, providing a narrow emission.

5.4 $\text{Ca}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$

$\text{Ca}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ (nicknamed CLA) was first experimentally investigated by Pust et al. [29] in 2014, during the same year than the $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ investigation [28]. The structure presents similarities with $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$, with UCr_4C_4 type and one-dimensional cation channel. In addition to the replacement of Sr by Ca, the second shell environment of Ca atoms all contains two Li atoms and six Al atoms, in contrast to SLA where alternating numbers of Li/Al in the second shells are associated to two crystallographic Sr sites that the Eu atom can substitute. In CLA, a single Sr site is available.

5.4.1 ΔSCF calculations

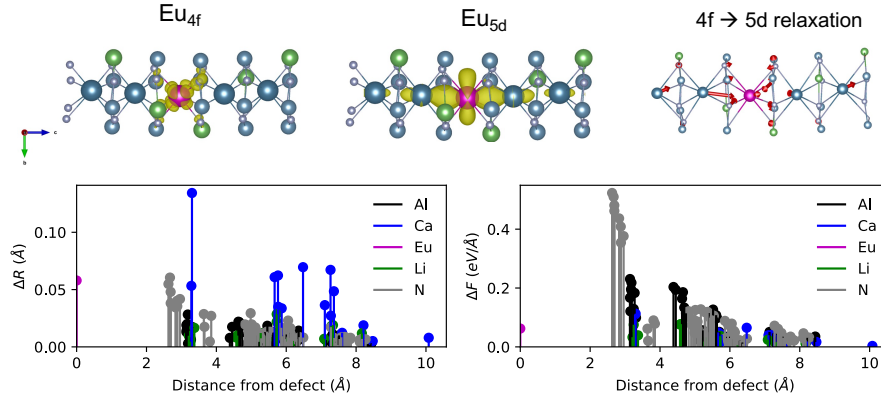


Figure 5.13: The probability density of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8\text{S}_{7/2})$ ground and lowest $4f^6(^7\text{F}_J)5d^1$ excited states in $\text{Ca}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$. On the right, a three-dimensional view of the displacements near the Eu activator accompanying the electronic transition, scaled by 20 for clarity. On the bottom, the norm of the atomic displacements ΔR and forces ΔF induced by the 5d to 4f transition as a function of the distance from Eu.

ΔSCF calculations have been performed on this material. Figure 5.13 presents the probability density associated to the highest occupied Kohn-Sham levels. A $\text{Eu}_{5d_{z^2}}$ state, aligned along the Ca channel, is stabilized in the excited state, in a similar fashion than in the Sr channels of SLA, SLO and SALON. The atomic relaxations show hence similar patterns ; a Eu- N_8 cuboid contraction (when going from 4f to 5d),

accompanied by a long-range channel Sr displacements. Similarly to $\text{SrLiAl}_3\text{N}_4$ and $\text{Sr}[\text{Li}_3\text{AlO}_4]:\text{Eu}^{2+}$, the first-shell cuboid is not perfectly symmetric and leads to a net displacement of the Eu atom. This also means that the Sr atoms are not moving perfectly aligned to the Sr channel. The magnitude of these displacements are shown on figure 5.13 as a function of the distance from the Eu dopant. The forces exerted on the atoms in the unrelaxed ground state are also presented. The table 5.4 decomposes the total normal coordinate change ΔQ^2 of each site into the different species present in the structure, and allows a quick comparison with the other UCr_4C_4 phosphors studied in this work. This table and the associated discussion on this decomposition can be found in the section 5.5, at the end of this chapter.

5.4.2 Huang-Rhys spectral function

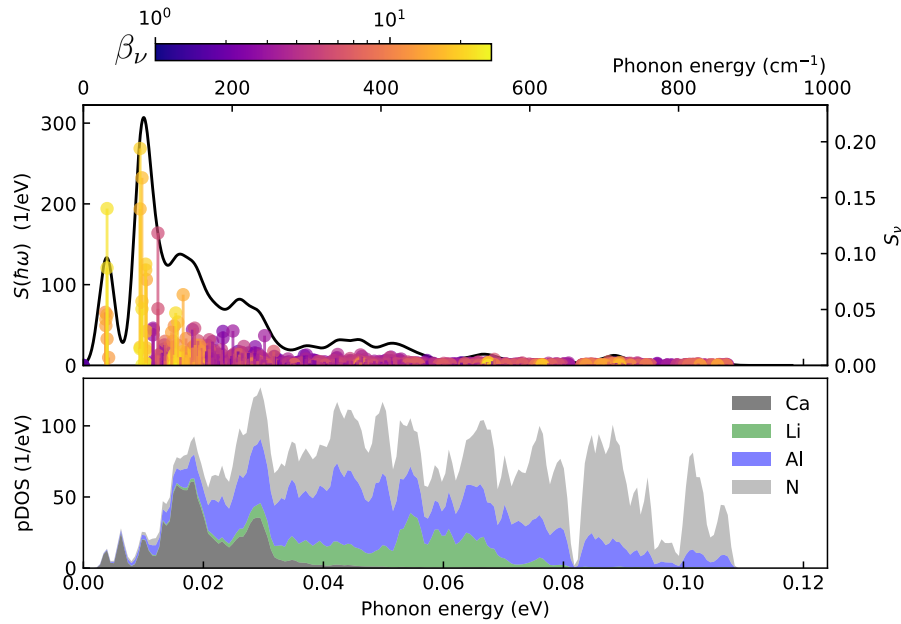


Figure 5.14: Top : the Huang-Rhys spectral $S(\hbar\omega)$ (black line) obtained from the individual S_v (vertical lines), using a 2 meV gaussian broadening for visualization. Each vertical line is colored according to the localization ratio of the mode β_v . Bottom : atom-projected phonon density of states.

The Huang-Rhys spectral decomposition is presented in figure 5.14 and is computed with a 576 atoms supercell with the embedding

procedure (but only with bulk phonons, corresponding to a cut-off radii of $R_c=0\text{\AA}$). Such a decomposition reveals that the coupling modes present the same characteristic than in other UCr_4C_4 . Indeed, the atom-projected phonon density of states of figure 5.14 makes clear that the electron-phonon coupling associated with the 5d-4f transition is dominated by Ca low-energy modes. These modes, as in SALON and SLA (site 1), are collective displacements of Ca atoms along the 1D Ca chain that couples strongly with the above-described 5d-4f relaxation of the Ca channel containing Eu.

5.4.3 Photo-luminescence lineshape

The PL lineshape is computed based on the Huang-Rhys spectral function and compares well with the experiment at $T=300\text{K}$, see figure 5.15. The theoretical 0K spectrum is indicatively shown. No shift was applied for these spectra. The fact that the $T=0\text{K}$ spectrum matches very well the tail of the experimental $T=300\text{K}$ spectrum is fortuitous.

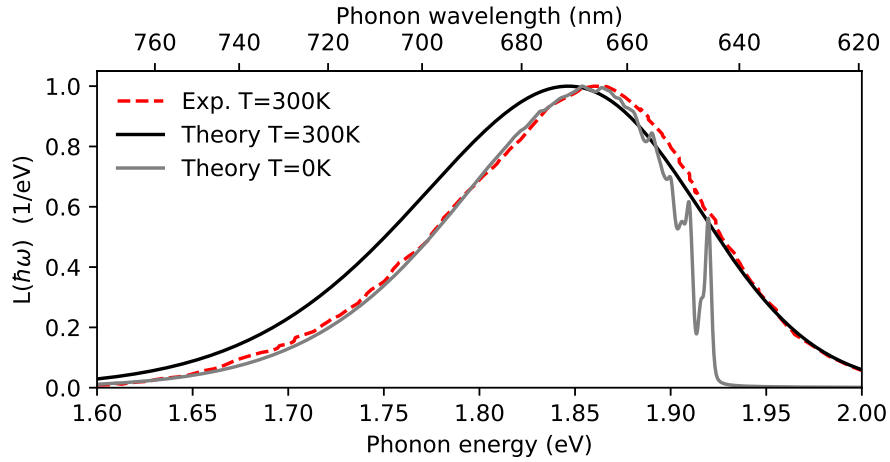


Figure 5.15: Experimental ($T=300\text{K}$) [29] and theoretical PL spectrum of $\text{Ca}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ at $T=0\text{K}$ and $T=300\text{K}$.

5.5 DISCUSSION AND CONCLUSION ON UCr_4C_4 PHOSPHORS

Let us take a step back and extract trends from the results obtained for UCr_4C_4 -type phosphors. Table 5.3 presents a summary of the computed parameters entering the one-dimensional configuration coordinate model for the seven phosphors studied in this work. The first six rows correspond to UCr_4C_4 -type phosphors, with the two non-equivalent Sr sites for the case of $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ and $\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}$. A common atomic displacement pattern is observed in these structures when transitioning from the ground to the excited state: first, an expansion of the first-coordination shell of Eu, composed of O and/or N atoms; second, a long-range relaxation of the cation (Sr-Ca) atoms in the channel containing the Eu atom, towards this Eu atom; and third, if the cuboid Eu shell is asymmetric, the Eu atom moves within its cage. An exception is noted for the $\text{Eu}(\text{Sr}_2)$ site in $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$, where the Sr displacements are smaller and significant displacements are observed in the second-shell Al atoms. This is due to the fact that, unlike in other materials, the excited state does not correspond to a $\text{Eu}_{5d_{z^2}}$ -like state aligned along the cation channel. Regarding the zero-phonon line

	ΔQ (amu ^{1/2} Å)	ΔR (Å)	E_{FC} (meV)	E_{ZPL} (eV)	ω_{eff} (meV)	S
$\text{CaLiAl}_3\text{N}_4:\text{Eu}^{2+}$	1.372	0.237	87.316	1.920	19.687	4.435
$\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}\text{-1}$	1.069	0.163	72.361	1.916	23.018	3.144
$\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}\text{-2}$	1.060	0.223	112.322	1.990	28.903	3.886
$\text{SrLi}_2\text{Al}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$	1.127	0.225	96.066	2.032	25.152	3.819
$\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}\text{-1}$	1.731	0.249	121.389	2.266	18.400	6.597
$\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}\text{-2}$	2.436	0.348	152.823	2.462	14.673	10.415
$\text{SrCl}_2:\text{Eu}^{2+}$	1.308	0.206	72.560	3.395	18.824	3.855
$\text{CaSO}_4:\text{Eu}^{2+}$	0.838	0.190	47.541	3.800	23.786	1.999
$\beta\text{-SiAlON}:\text{Eu}^{2+}$	0.667	0.138	97.317	2.676	42.740	2.277

Table 5.3: Summary of the computed parameters entering the one-dimensional configuration coordinate model for the seven phosphors studied in this work. The first six rows are for UCr_4C_4 -type phosphors.

energies, a blue-shift trend is correctly observed when moving from nitride to oxide environments surrounding the Eu atom, emphasizing

the importance of the first coordination shell in determining transition energies.

The effective coupling frequency ω_{eff} is relatively small (compared to the maximum available phonon frequencies) in all of the UCr_4C_4 structures studied, though with some variation (e.g., the difference between sites 1 and 2 in $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$). This behavior can be attributed to the fact that, in these structures, the Huang-Rhys spectral function is predominantly shaped by the coupling with low-frequency phonons, which involve collective displacements of the Ca-Sr atoms along the cation channel containing the Eu atom. These modes are either localized (especially if a net force is exerted on the Eu atom during the electronic transition) or delocalized, bulk-like phonon modes. Although one might initially expect modes involving O/N atoms to

	ΔQ_{Eu}^2	$\Delta Q_{\text{Sr-Ca}}^2$	ΔQ_{Li}^2	ΔQ_{Al}^2	$\Delta Q_{\text{O-N}}^2$	$\Delta Q_{\text{total}}^2$
$\text{CaLiAl}_3\text{N}_4:\text{Eu}^{2+}$	0.345 (18.32%)	1.135 (60.28%)	0.019 (1.01%)	0.132 (7.01%)	0.253 (13.44%)	1.883 (100.0%)
$\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}-1$	0.277 (24.26%)	0.588 (51.49%)	0.007 (0.61%)	0.068 (5.95%)	0.202 (17.69%)	1.142 (100.0%)
$\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}-2$	0.099 (8.81%)	0.217 (19.31%)	0.02 (1.78%)	0.366 (32.56%)	0.422 (37.54%)	1.124 (100.0%)
$\text{SrLi}_2\text{Al}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$	0.0 (0.0%)	0.565 (44.49%)	0.027 (2.13%)	0.156 (12.28%)	0.522 (41.1%)	1.27 (100.0%)
$\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}-1$	1.383 (46.13%)	0.998 (33.29%)	0.057 (1.9%)	0.074 (2.47%)	0.486 (16.21%)	2.998 (100.0%)
$\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}-2$	2.13 (35.89%)	2.674 (45.06%)	0.12 (2.02%)	0.148 (2.49%)	0.861 (14.51%)	5.934 (100.0%)

Table 5.4: The square of the total normal coordinate change ΔQ^2 decomposed by species in the UCr_4C_4 -type phosphors studied in this work.

play a significant role due to the Eu-O/N environment, it turns out that they contribute less to the spectral function than Eu-Ca-Sr modes. This is quantitatively demonstrated in Table 5.4, which decomposes the square of the normal coordinate change ΔQ^2 into contributions from

different species. The table shows that the displacement of Eu (ΔQ_{Eu}^2) can be significant (up to 46.13% in $\text{SrLi}_3\text{AlO}_4\text{:Eu}^{2+}\text{-1}$) in asymmetric Eu-O/N environments, while the cation channel displacement ($\Delta Q_{\text{Sr-Ca}}^2$) is predominant in all structures (except in $\text{SrLiAl}_3\text{N}_4\text{:Eu}^{2+}\text{-2}$, as explained earlier).

It is important to note that the ΔQ values are extracted from the "small" ΔSCF supercell, meaning that the raw values are indicative of trends between the structures. Increasing the supercell size using the embedding methodology would further accentuate the contribution of the Sr-Ca atoms, which exhibit long-range displacements.

We note also that although ΔR is always positive (see equation 1.2), we need to remember that the Eu-ligand distance actually contracts when going from the ground to the excited state, in contrast to the common intuition.

In conclusion, the small FWHM of the emission spectrum in these UCr_4C_4 phosphors can be directly linked to their particular structure. A small FWHM is achieved by simultaneously reducing both the normal coordinate change ΔQ and the effective frequency ω_{eff} . The small ΔQ arises from the high rigidity of the UCr_4C_4 host structure, while the small effective frequency results from the strong coupling between the cation channel relaxation and low-frequency phonon modes. While the rigid nature of these host structures has been previously noted in earlier studies (e.g., refs [28, 32, 38]) to explain the narrow emission, the identification of long-range relaxation patterns along the channels and the coupling with low-frequency modes represents a major contribution of this PhD work. At this stage, we have advanced the understanding between the property (the narrow emission) and the structural feature (the one dimensional cation chain) but it is difficult to suggest from scratch new interesting stable inorganic phosphors based on this observation. It is our hope that this will help in the discovery of new unknown narrow-emission phosphors.

VIBRONIC FINGERPRINT OF SELECTED EU-DOPED PHOSPHORS

In this chapter, I present the results of computational investigations conducted on three phosphor materials, focusing on their luminescent properties. The methodology applied follows the methodology outlined in the introduction of the previous chapter.

First, $\text{SrCl}_2\text{:Eu}^{2+}$ and $\text{CaSO}_4\text{:Eu}^{2+}$ are investigated. They are of interest due to the clear vibronic features observed in their photoluminescence (PL) spectra at low temperatures. Although these materials are currently not used much for technological application, they are valuable for examining the theoretical frameworks applied in this study.

Additionally, $\beta\text{-SiAlON:Eu}^{2+}$, a widely studied green-emitting phosphor with both technological and theoretical relevance, is included for its distinctive luminescent behavior. This material is well-known for its application in WLEDs, but uncertainties remain regarding the exact location of the Eu^{2+} ion within the host lattice. The clear vibronic features at low temperatures offer an opportunity to test the structural models proposed in the literature.

Lastly, the investigation of CaO:Eu^{2+} , for which the methodology applied did not produce the expected results, is presented as an example of the limitation of the approach. The reasons for the discrepancies are not yet fully understood, and this issue will be discussed.

6.1 $\text{SrCl}_2:\text{Eu}^{2+}$

In cubic SrCl_2 ($\text{Fm}\bar{3}\text{m}$), the Eu^{2+} ion substitutes Sr on the eight-coordinate cubic symmetry site. The emission spectrum has been experimentally reported for small Eu concentration at 10K [154]. Clear vibrational progressions are observed and the material constitutes an interesting test case for the methodology used in this thesis, because of its simplicity : a cubic structure with textbook cubic Eu-Cl_8 environment. It is noted that a Huang-Rhys fitting was proposed in reference [154] to explain the emission spectrum. Using a three-mode model with $S_0 = 3.35$, $\omega_0 = 143\text{cm}^{-1}$, $S_1 = 1.28$, $\omega_1 = 209\text{cm}^{-1}$, and $S_2 = 0.35$, $\omega_2 = 113\text{cm}^{-1}$, a reasonable agreement is obtained.

6.1.1 ΔSCF calculations

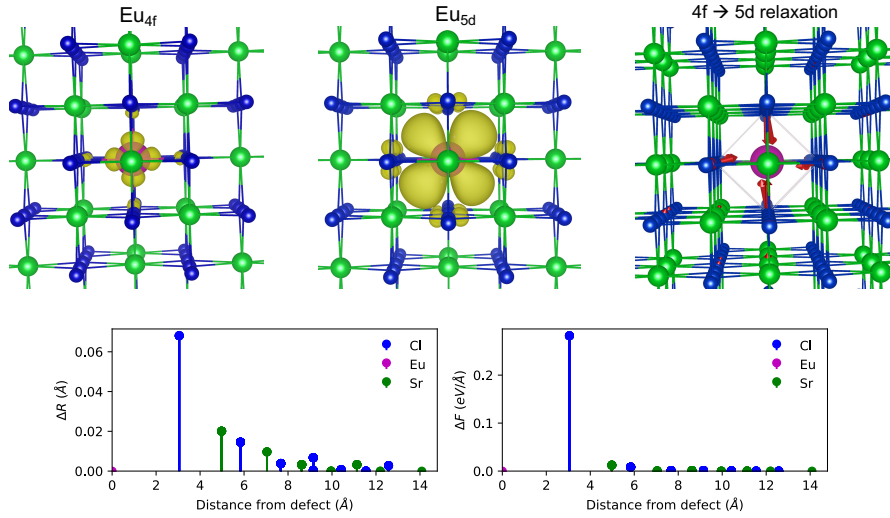


Figure 6.1: The density probability of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8\text{S}_{7/2})$ ground and lowest $4f^6(^7\text{F}_J)5d^1$ excited states in $\text{SrCl}_2:\text{Eu}^{2+}$. On the right, a three-dimensional view of the displacements near the Eu activator, scaled by 20 for clarity. On the bottom, the norm of the atomic displacements ΔR and forces ΔF induced by the $5d$ to $4f$ transition as a function of the distance from Eu.

Figure 6.1 presents the density probability associated to the highest occupied Kohn-Sham levels. The Eu_{5d} -like orbital has lobes pointing towards the faces of the Eu-Cl_8 cube, avoiding the Cl^{2-} ions. The atomic relaxation is shown on the same figure. It consists first of a

textbook pattern of symmetric shrinking of the Eu-Cl_8 . The excited state Eu-Cl distance (2.98 Å) is shorter than the ground state Eu-Cl distance (3.05 Å), as observed in other Eu^{2+} phosphors. Outside this first-coordination shell, the atoms also move towards the Eu atom, with decreasing displacement as the distance from Eu increase (figure 6.1 bottom left). It is interesting to see that these long-range displacements, that extend up to 10 Å from the Eu atom, are actually caused by very localized forces acting on the eight first Cl atoms (figure 6.1 bottom right) in a kind of avalanche effect. Outside this first shell, the forces are essentially zero.

6.1.2 Huang-Rhys spectral function

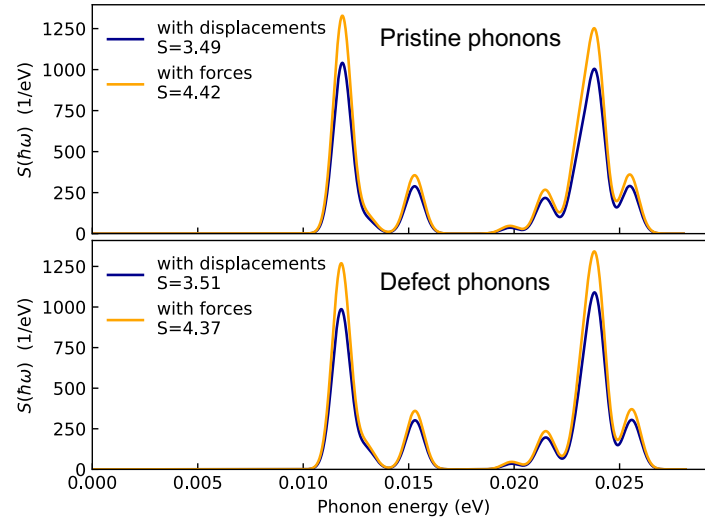


Figure 6.2: Huang-Rhys spectral function of $\text{SrCl}_2:\text{Eu}^{2+}$ computed in a small 81 atom supercell, allowing to compare the use of the forces vs the displacements when computing the partial Huang-Rhys factors S_i . For both defect and pristine phonons, the use of the forces overestimate the total Huang-Rhys factor.

The Huang-Rhys spectral function was first computed in a small supercell of 81 atoms in order to compare the use of the displacements (equation 3.7) with the use of the forces (equation 3.9). The result is presented on figure 6.2 for defect and bulk phonons. While the peak positions and relative intensities are similar, the total Huang-Rhys factor (integrated Huang-Rhys spectral function) is overestimated when using

the forces. When using the defect phonons, the use of the displacements gives $S=3.51$ and $S=4.37$ for the forces. Since equations 3.7 and 3.9 are equivalent under the harmonic approximation, this overestimation is a direct measure of the validity of the harmonic hypothesis (in the sense that atoms vibrates in a purely multi-dimensional quadratic potential). For a given cell size, the use of equation 3.7 (with the displacements) is better since it includes anharmonic behavior. On the other hand, the use of equation 3.9 (with the forces) has the advantage to yield a better convergence with respect to the supercell size, in the harmonic regime. In the case of $\text{SrCl}_2:\text{Eu}^{2+}$, it seems that a non-negligible anharmonic behavior is present. A convergence of the Huang-

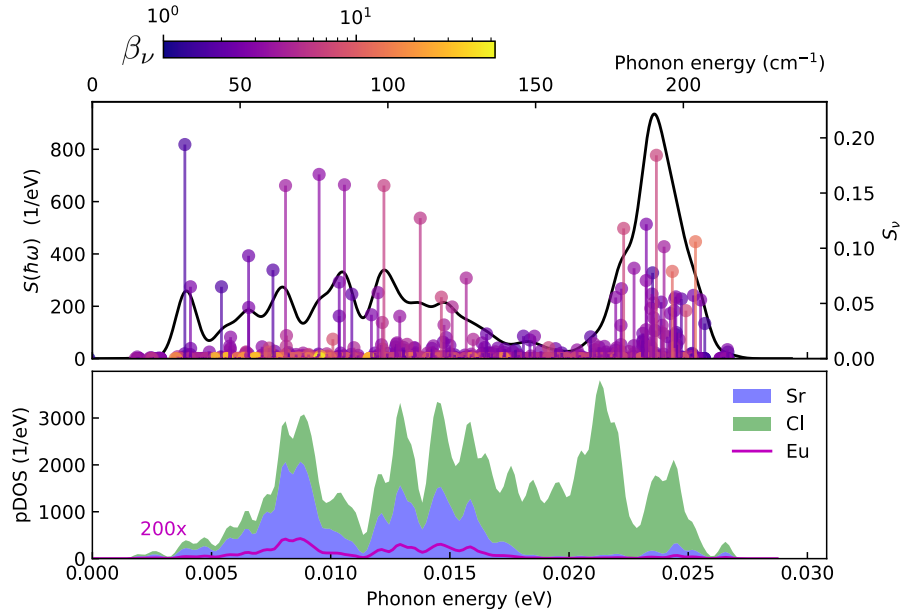


Figure 6.3: Top : the Huang-Rhys spectral $S(\hbar\omega)$ (black line) obtained from the individuals S_ν (vertical lines) in a 3000-atom supercell, using a 2 meV gaussian broadening for visualization. Each vertical line is colored according to the localization ratio of the mode β_ν . Bottom : atom-projected phonon density of states.

Rhys (HR) spectral function with respect to the number of atoms in the "phonon" supercell was presented earlier in this thesis in figure 3.11. From 81-atom supercell to 3000-atom supercell, it was shown that the coupling with high-frequency modes quickly converges while the convergence of the coupling with long-wavelength modes is harder to

achieve. The total HR factor slowly converges to $S=5.29$ for the largest cell (obtained with the forces), see figure 3.11 right.

The HR spectral function computed with a 3000-atom supercell is shown on figure 6.3. We observe that no true local mode couples with the transition. Instead, a series of pseudo-local modes, involving Cl atoms, with $\beta_v \approx 10$ are present at high frequency. Because the Eu atom remains static during the electronic transition, no Eu-based local mode is observed in the HR spectral function.

6.1.3 Photo-luminescence lineshape

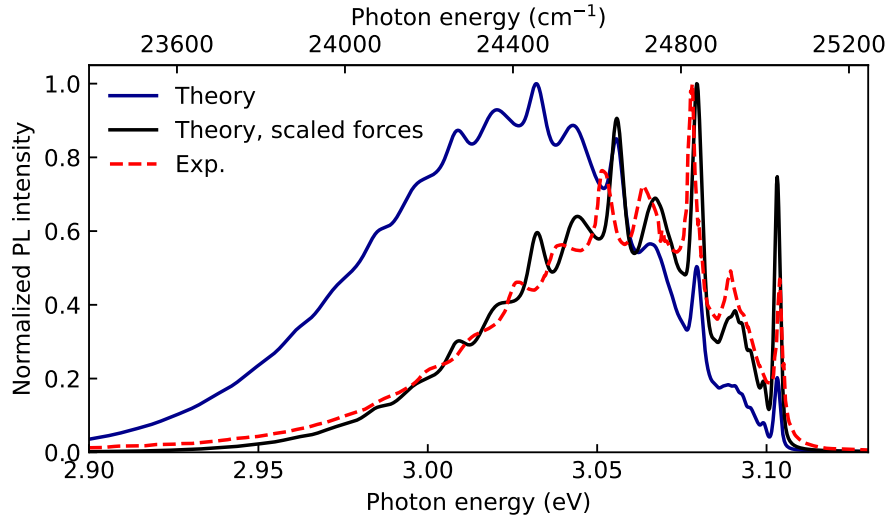


Figure 6.4: Experimental [154] and theoretical PL spectrum of $\text{SrCl}_2:\text{Eu}^{2+}$ ($T=10\text{K}$). The theory ($S=5.29$) does not reproduce well the relative intensities of the vibronic peaks. Scaling the forces by 0.8 ($S=3.387$) restore the agreement between theory and experiment. The overestimation of the forces, and consequently the overestimation of the Huang-Rhys factor, might be due to anharmonicities, as discussed in the text.

The PL lineshape is computed based on the Huang-Rhys spectral function presented in the previous section and is compared with the experiment at $T=10\text{K}$, see figure 6.4. The ZPL energies are aligned in order to compare the vibronic progression (a rigid shift of 0.29 eV is applied). While the peak positions are correctly captured, their intensities are not (see blue curve). It appears that the total Huang-Rhys factor ($S=5.29$) is overestimated. Indeed, if we scale all the forces by a

constant factor $f = 0.8$, a much improved agreement is obtained (black curve). With such scaling, $S=3.387$. The reason for this overestimation of the forces remains unclear. We believe that the need for this scaling factor partly comes from the non-harmonic behaviors observed in this system. Indeed, it has been shown above in a smaller supercell that the lack of harmonicity led to an overestimation of the total HR factor.

6.2 $\text{CaSO}_4:\text{Eu}^{2+}$

In the orthorhombic (almost tetragonal) $\text{CaSO}_4:\text{Eu}^{2+}$ (Cmcm), the Eu^{2+} ion substitutes the Ca atom in a distorted O_8 polyhedron. The emission spectra have been reported experimentally for small Eu concentration [169] at 8K, 80K and 300K. As for SrCl_2 , clear vibrational progressions are observed and the material constitutes an interesting study-case for the methodology used in the case of an asymmetric Eu environment.

6.2.1 ΔSCF calculations

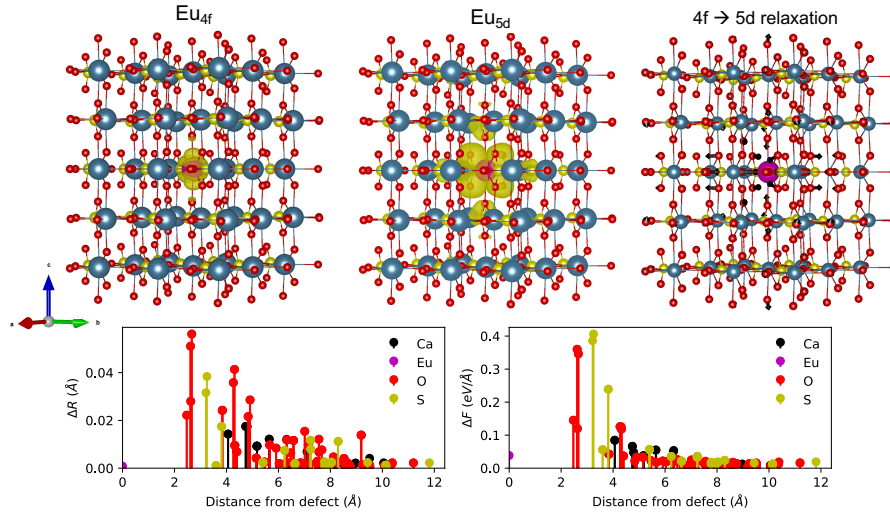


Figure 6.5: The probability density of the highest occupied Kohn-Sham orbitals associated to the $4f^7(^8\text{S}_{7/2})$ ground and lowest $4f^6(^7\text{F}_J)5d^1$ excited states in $\text{CaSO}_4:\text{Eu}^{2+}$. On the right, a three-dimensional view of the displacements near the Eu activator accompanying the electronic transition, scaled by 20 for clarity. On the bottom, the norm of the atomic displacements ΔR and forces ΔF induced by the $5d$ to $4f$ transition as a function of the distance from Eu.

Figure 6.5 presents the probability density associated to the highest occupied Kohn-Sham levels in ground and excited state. Interestingly, the $5d$ -like orbital hybridizes with O and S p -states along the c -axis. The atomic relaxation shows a complex pattern and is shown on the same figure. First, the distorted Eu-O_8 polyhedron shrinks: the mean excited state Eu-O distance (2.557 Å) is shorter than the mean ground state Eu-O distance (2.593 Å), as observed in other Eu^{2+} phosphors. Outside

this first-coordination shell, the displacements pattern is anisotropic: in the a-b plane, some O atoms are pushed away from Eu, while other O and S atoms move towards the Eu. Along the c-axis, we observe an interesting collective displacement of the O atoms along a 1D chain. Notice also that the asymmetry of the Eu-O₈ polyhedron causes the Eu atom to slightly displace with the transition. As for SrCl₂:Eu²⁺, the decay of the displacements and forces are presented on the bottom of figure 6.5.

6.2.2 Huang-Rhys spectral function

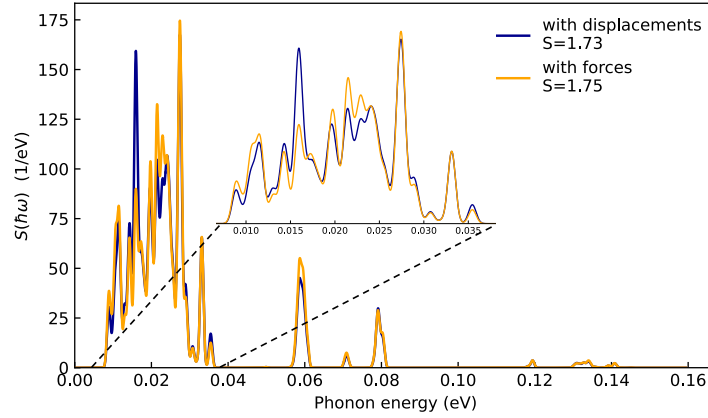


Figure 6.6: Huang-Rhys spectral function computed in a 216 atoms supercell, allowing to compare the use of the forces vs displacements when computing the partial Huang-Rhys factors S_ν . Both approaches leads to similar Huang-Rhys factor, indicating a strong validity of the harmonic approximation.

The Huang-Rhys spectral function was first computed in a small supercell of 216 atoms in order to compare the use of the displacements (equation 3.7) with the use of the forces (equation 3.9). The result is presented on figure 6.6. When using the defect phonon, the use of the displacements gives $S=1.73$ and $S=1.75$ for the forces. This indicates a good validity of the harmonic approximation in this system, ensuring also that the use of the forces in large supercells would very well approximate displacements in these large supercells. A convergence of the Huang-Rhys (HR) spectral function with respect to the number of atoms in the "phonon" supercell is presented on figure 6.7 from 216-atom supercell to 2592-atom supercell. Notice that the variation of the total normal coordinate change ΔQ and effective frequency ω_{eff}

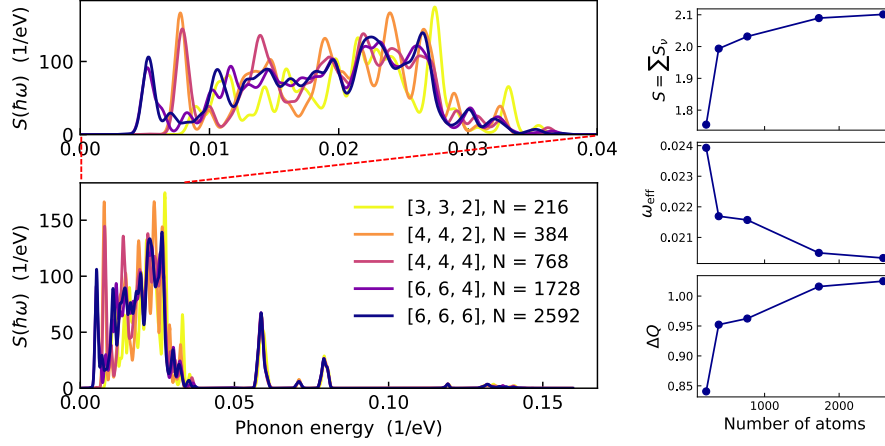


Figure 6.7: Convergence of the Huang-Rhys spectral function as a function of the size of the large phonon supercell in $\text{CaSO}_4:\text{Eu}^{2+}$ for defect phonon obtained with the embedding methodology. A zoom at low frequency is provided.

with the number of atoms is not as smooth as in the case of $\text{SrCl}_2:\text{Eu}^{2+}$ because the supercell size can be increased along the c-axis or within the a-b plane.

The HR spectral function computed with the largest supercell used ($6 \times 6 \times 6$, 2592 atoms) is shown on figure 6.8, alongside the atom-projected phonon density of states. We observe that most of the coupling appears at low-frequency. Two modes are indicatively displayed in the inset. The first is a bulk-like acoustic mode with a small contribution on the Eu atom. The second lies at higher energy (77 meV) and is a purely local mode presenting a complex pattern of displacements, mostly localized in the a-b plane. It involves a distortion of the Eu-O_8 polyhedron, and displacements of the second-shell O and S atoms. We note that the peak at around 60 meV corresponds to oxygen modes moving along the c-axis.

6.2.3 Photo-luminescence lineshape

The PL lineshape is computed based on the Huang-Rhys spectral function for various temperatures and compared to experimental data, see figure 6.9. The ZPL energies are aligned with a rigid shift of 0.55 eV in order to compare the vibronic progression. The agreement is satisfactory: the vibronic peaks are well reproduced with good relative

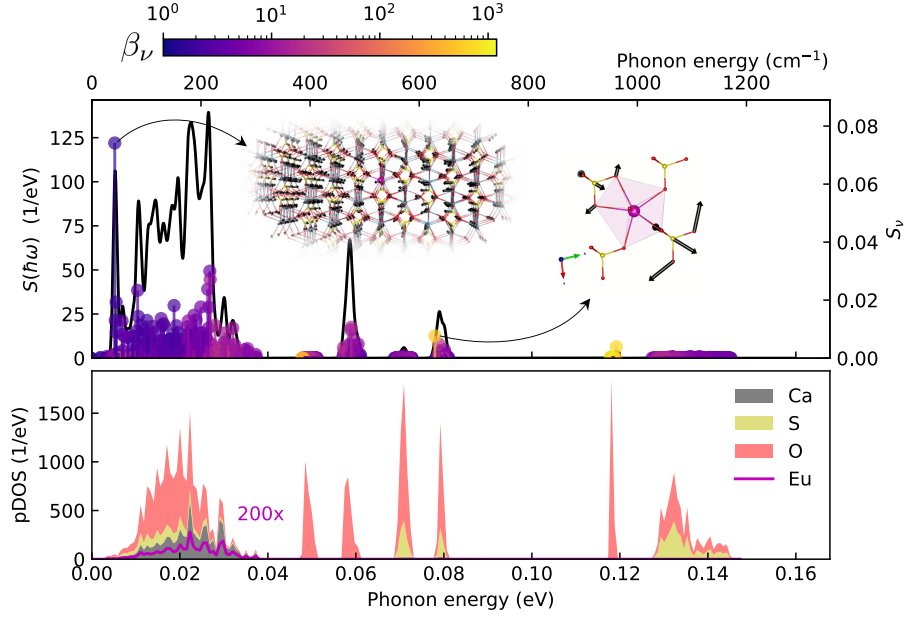


Figure 6.8: Top : the Huang-Rhys spectral $S(\hbar\omega)$ (black line) obtained from the individual S_v (vertical lines) in a 2592-atom supercell, using 1 meV gaussian broadening for visualization. Each vertical line is colored according to the localization ratio of the mode β_v . Bottom : atom-projected phonon density of states. The Eu-projected DOS has been multiplied by 200, for visualization.

intensities. This indicates that the above-mentioned results provide a good physical description of the luminescent processes in $\text{CaSO}_4:\text{Eu}^{2+}$. We still note a small offset between calculations and experiments for the two peaks originating from the coupling with phonons at 77 meV and 60 meV. It is believed that this is due to an underestimation of these phonon frequencies by PBE functional [170, 171].

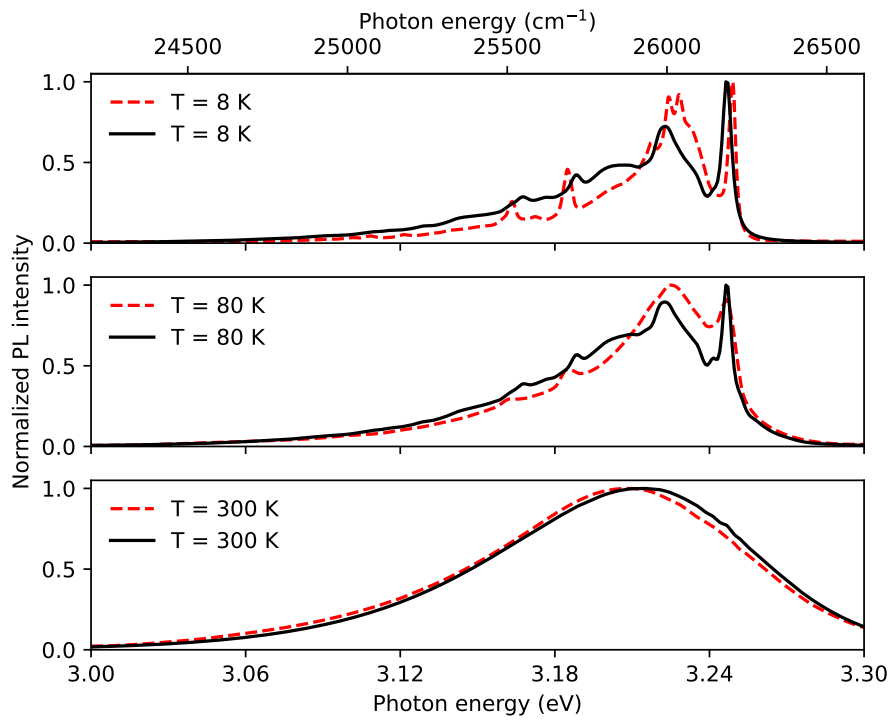


Figure 6.9: Experimental [169] and theoretical PL spectrum of $\text{CaSO}_4:\text{Eu}^{2+}$ for various temperatures ($T=8\text{K}$, 80K , 300K). A shift of 0.55 eV was applied to align the ZPL energies.

6.3 β -SiAlON:Eu²⁺

This section will likely be the subject of a future publication tentatively entitled : *Bouquiaux et. al*, "A first-principles confirmation of the Eu location in low-z Si_{6-z}Al_zO_zN_{8-z}:Eu²⁺ green phosphor through vibronic analysis".

β -SiAlON:Eu²⁺ stands out as a promising green-emitting material due to its high quantum efficiency, narrow emission bandwidth, and thermal stability, making it particularly suitable for high-power LED applications and liquid crystal display (LCD) [172–174]. The β -SiAlON structure is derived from β -Si₃N₄, with Al substitution for Si and O substitution for N, maintaining the charge neutrality of the host lattice. This results in the general chemical formula Si_{6-z}Al_zO_zN_{8-z}, where z controls the degree of substitution. Doping with Eu²⁺ introduces green luminescence, driven by the 5d-4f transitions. The characteristic emission typically peaks around 535 nm, with a FWHM ranging between 45 and 55 nm, which is essential for high-color-purity applications [172, 174, 175].

Despite its technological significance, the precise local coordination environment of Eu²⁺ in β -SiAlON remains an open question. It has been recognized early that a substitution is unlikely, due to the size mismatch between Eu²⁺ and the cations in the structure, meaning that the ion Eu²⁺ might occur at an interstitial site [177]. Experimental works using scanning transmission electron microscopy (STEM) confirmed that the Eu²⁺

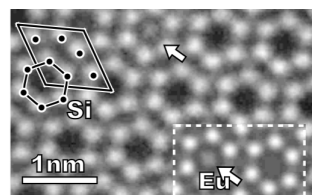


Figure 6.10: STEM images of β -Si₃N₄. Reproduced with permissions from reference [176].

occupies interstitial sites within the large hexagonal channels of the β -Si₃N₄ framework [176], as shown in figure 6.10. Extended X-ray absorption fine structure (EXAFS) measurements suggested later, in 2014, that the Eu²⁺ ion occupies a distorted 12-fold coordinated environment within these hexagonal channels [177]. However, experimental information about the detailed cation/anion ordering in β -Si₃N₄ remains difficult to obtain due to the almost indistinguishable scattering factors of the two substitution pairs, Al³⁺/Si⁴⁺ and O²⁻/N³⁻, and the low concentration of the Eu activator [177].

In 2016, the Eu-N₁₂ environment hypothesis was challenged by first principles calculations designed to provide chemical rules for the β -

SiAlON:Eu²⁺ [178]. It was shown that the energetically favored location within the c hexagonal channel leads to a Eu-N₉ polyhedron. This study proposed several structural models, for various z concentrations. Regarding the Al/O locations, they found that the energy is minimized if (i) all O are in 2c Wyckoff site, (ii) all O have at least one Al neighbor and (iii) All Al, O, and Eu must be in the same (001) a-b plane.

In 2017, it was recognized that trends in distortion of the luminescent center explain the experimentally observed red shift, emission broadening, and increasing thermal stability with increasing z value only if a Eu-N₉ polyhedron is considered [179], agreeing with the conclusions of the 2016 study.

Several studies have measured the PL spectrum for various z concentrations as illustrated on figure 6.11 (a) at room temperature [180]. Increasing z value leads to a red-shift of the emission peak. It is believed that larger z increasingly distorts the Eu-N₉ environment, because of the growing number of potential O/Al substitutions near the Eu atom. This would result in an increased crystal field splitting, explaining the red-shift [178, 179]. Low temperature measurements (6K) revealed clear vibronic progressions for low-z value (z = 0.025) [180], as reproduced on figure 6.11 (b). The temperature dependence of such PL spectrum was studied later for z = 0.031 and is presented on figure 6.11 (c).

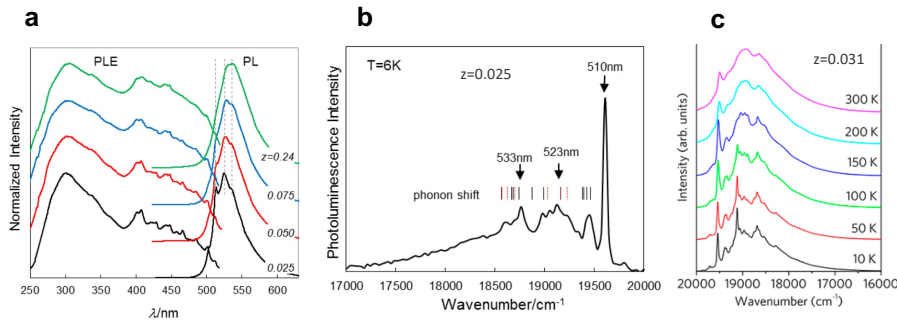


Figure 6.11: (a) Room-temperature PL spectrum of β -Si_{6-z}Al_zO_zN_{8-z}:Eu²⁺ for various z values. (b) 6K PL spectrum at low z=0.025. (c) Temperature dependence of the PL spectrum for z=0.031. Adapted with permissions from reference [180] (a and b) and from reference [181] (c).

In this work, the aim is to build upon the results of these different works to bring new insights on the precise location of the Eu²⁺ in the structure. We extract the low-z model structure obtained in reference [178], in which the most stable arrangement of Al-O substitution and energetically favored Eu position in the β -Si₃N₄ host was computed

with DFT. The structure is pictured on figure 6.12, with a cut in the Eu-Al-O plane. Note that the number of O and Al atoms is different because of the need to charge balance the Eu^{2+} interstitial. The Eu^{2+} PL lineshape is obtained by virtue of ΔSCF -constrained occupation method, feeding a multi-phonon mode Huang-Rhys model. The phonon modes of large defect supercells (including the Eu interstitial, the Si/Al and N/O substitutions) are obtained through the IFCs embedding method. Comparison between the spectrum obtained with this first-principles technique and with experiment allows us to confirm the validity of the model structure used.

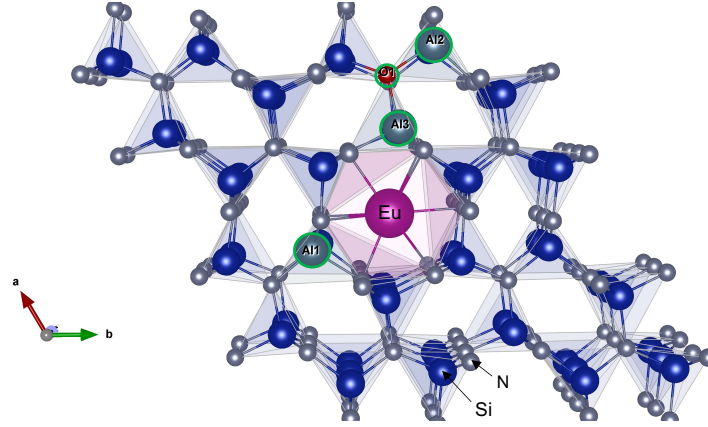


Figure 6.12: Model structure used in this work to simulate the PL spectrum of low- z $\beta\text{-SiAlON}:\text{Eu}^{2+}$, with a cut in the Eu-Al-O plane.

6.3.1 ΔSCF calculations

ΔSCF constrained occupations calculations were carried out on the model structure containing 225 atoms, with one Eu interstitial, three Al:Si and one O:N substitution. The structure is a $2 \times 2 \times 4$ supercell of the hexagonal $\beta\text{-Si}_3\text{N}_4$ ($P6_3/m$), containing 14 atoms per unit-cell. This gives a net composition of $\text{Si}_{93}\text{Al}_3\text{ON}_{127}:\text{Eu}$ or $z=0.1875$ while experimental low- z $\beta\text{-SiAlON}:\text{Eu}^{2+}$ reaches $z=0.025$. The Eu lies in a distorted Eu-N_9 environment with Eu-N distances varying from $2.48\text{\AA}$ to $2.83\text{\AA}$. Figure 6.13 (a) presents the probability density associated to the highest occupied Kohn-Sham levels in the ground and excited state, and the atomic relaxation induced by the transition, along two views. In panel (b), the energy levels are reported in the relaxed ground and excited

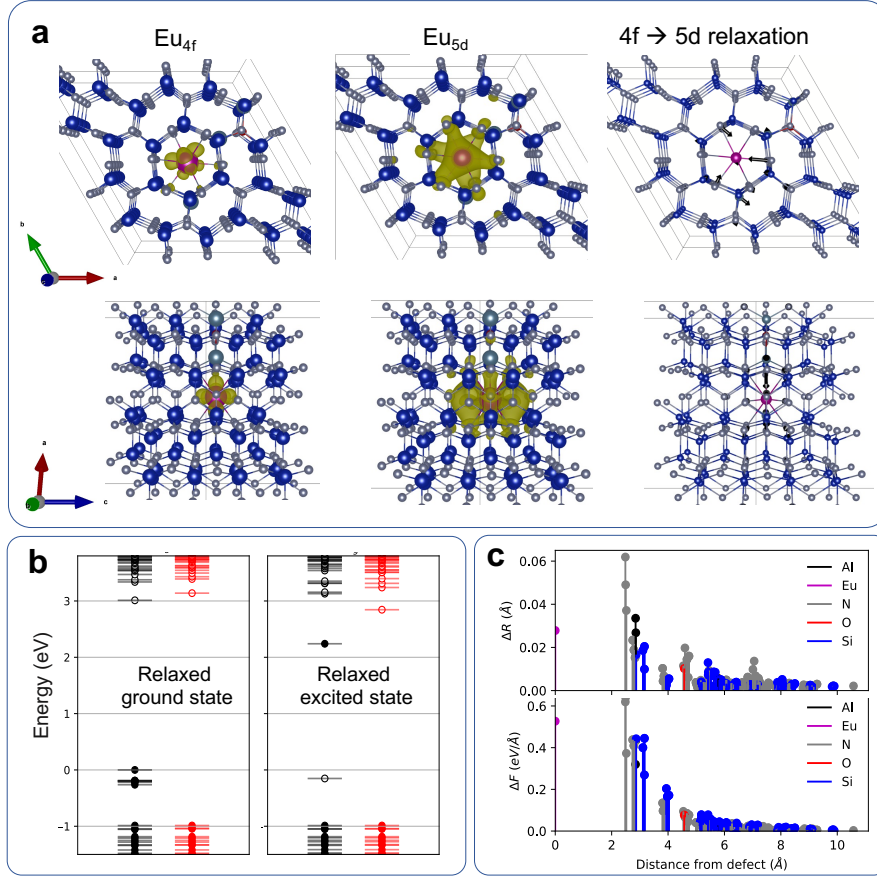


Figure 6.13: (a) Probability density associated with the Eu_{4f} and Eu_{5d} states. The atomic relaxation induced by the electronic transition is shown on the right. (b) Kohn-Sham energies computed in a relaxed 225-atom supercell at the PBE+U level, following the constrained occupation method. Black (red) lines refer to spin up (down) states. (c) Norm of the atomic displacements ΔR and forces ΔF induced by the 5d to 4f transition as a function of the distance from the Eu interstitial.

state. On the panel (c), the decay of the atomic displacements and forces are represented as a function of the distance from the Eu interstitial. The highest Eu_{4f} -like state detaches itself from the other Eu_{4f} states, a feature rarely observed in Eu-doped phosphors, though already reported in reference [178]. In the excited state, the Eu_{5d} -like orbital shows pronounced $5d_{z^2}$ character along the empty hexagonal channel. It is interesting to observe the three-fold symmetry of this state, which is rotated by 60° behind the Eu atom (see panel (a) middle top). A zero-

phonon line energy of 2.67 eV is computed, and should be compared with an experimental value of 2.43 eV for low- z β -SiAlON:Eu²⁺ [180].

Regarding the atomic relaxation caused by the electronic transition, it is first observed that the heavy Eu atom is significantly displaced in its Eu-N₉ environment, causing a global small shift of the Eu-N₉ polyhedron in the structure. It is expected that such a displacement impacts the luminescent properties as it is the mass-weighted relaxation that enters the equations. The Eu-N₉ polyhedron slightly shrinks, but in an anisotropic manner. Indeed, only the first three distant N atoms, contained in the a-b Eu-Al-O plane move toward the Eu atom by around 0.05 Å. A close inspection of these displacements also reveals that they are mostly contained in the a-b plane containing the Eu atom.

6.3.2 Unfolding the defect phonon band structure

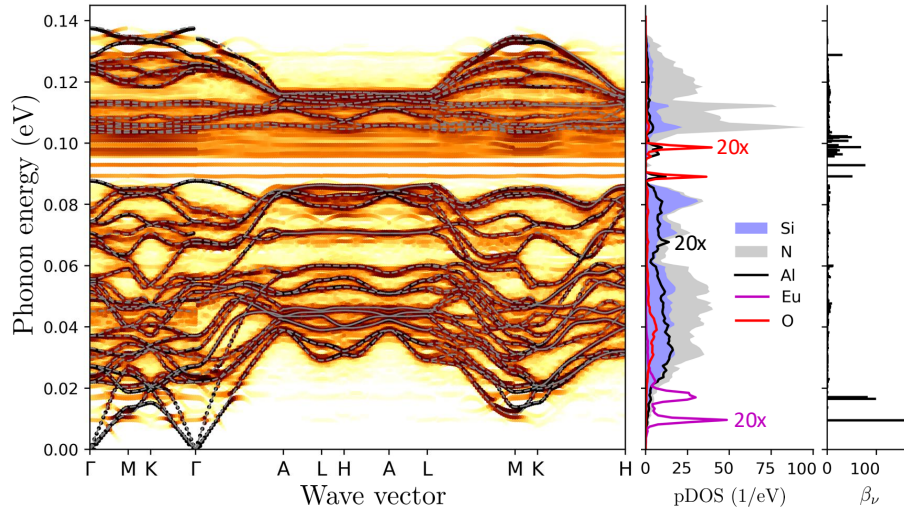


Figure 6.14: Unfolded phonon bands of β -SiAlON:Eu²⁺ with 0.4% Eu concentration projected on the high-symmetry momentum lines of the β -Si₃N₄ unit-cell (left). The color scale indicates unfolding weights: black (white) dots indicates weights approaching unity (zero). The phonon bandstructure of pristine β -SiAlON is shown in dashed-grey. The atom-projected density of states (middle) and the localization ratios of the modes (right). The contribution of Al, O and Eu atoms in the pDOS is multiplied by 20, for visualization.

The phonon modes of the model structure in its ground state are computed with the Phonopy package [148]. We use the unfolding technique (see references [109, 123]) to understand how the pristine

phonons of β -Si₃N₄ are perturbed by the introduction of the defect complex (one Eu interstitial, three Al and one O substitutions). Figure 6.14 presents the unfolded phonon bands of the 225-atom supercell on the high-symmetry q-path of the β -Si₃N₄ unit-cell. The color scale indicates unfolding weights: black (white) dots indicates weights approaching unity (zero). The phonon band structure of pristine β -Si₃N₄ is shown in dashed-grey. The atom-projected density of states and the localization ratios of the modes are presented on the same figure.

The colored unfolded bands allow one to observe the broadening of the pristine bands corresponding to slight perturbations of the pristine phonon modes. In addition, localized modes appear: at low frequency with Eu-based phonon modes, and in the gap of the pristine β -Si₃N₄ bands. These numerous in-gap modes involve the O and Al atoms.

6.3.3 Huang-Rhys spectral function

The convergence of the HR spectral function with respect to the number of atoms in the "phonon" supercell is presented on figure 6.15 from 225-atom supercell to 3501-atom supercell. The jump between the second and the third data-point comes from a change in the supercell size ratio (a/c). When using the defect phonon in the 225-atom supercell, the use of the displacements gives $S=1.98$ and $S=2.06$ for the forces, indicating the validity of the harmonic approximation in this system, and ensuring that the use of the forces in large supercells is well justified. The HR

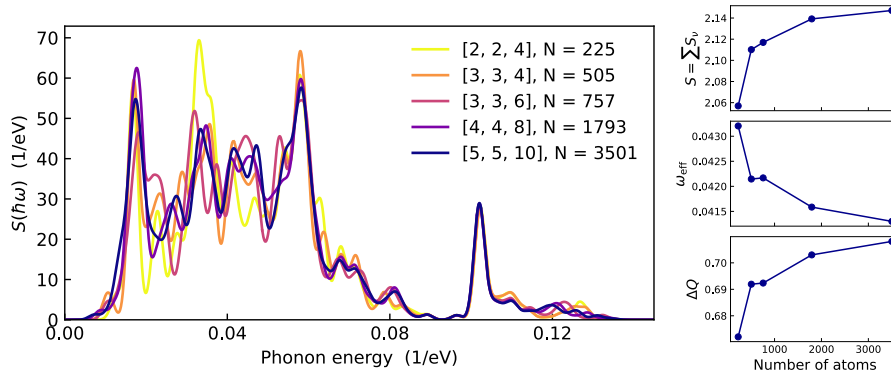


Figure 6.15: Convergence of the Huang-Rhys spectral function as a function of the size of the large phonon supercell β -SiAlON:Eu²⁺ for defect phonons obtained with the embedding methodology.

spectral function computed with a large $5 \times 5 \times 10$ supercell containing

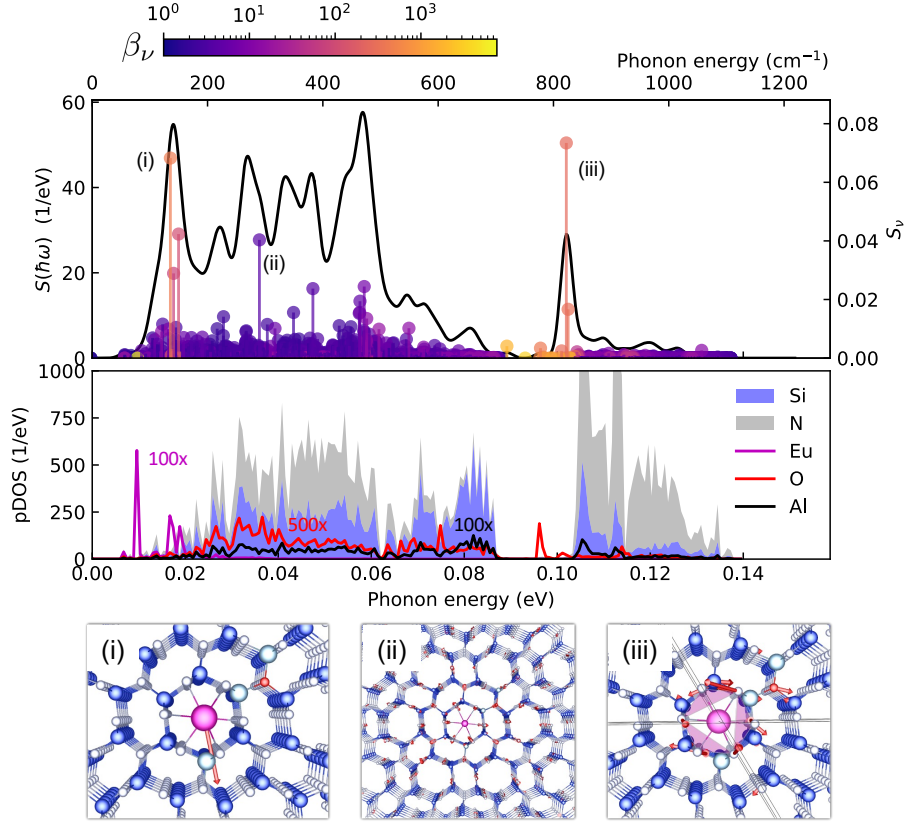


Figure 6.16: Top : the Huang-Rhys spectral $S(\hbar\omega)$ (black line) obtained from the individuals S_ν (vertical lines) in a 3501-atom supercell, using a 1 meV gaussian broadening for visualization. Each vertical line is colored according to the localization ratio of the mode β_ν . Bottom : atom-projected phonon density of states.

3501 atoms is shown on figure 6.16, alongside the atom-projected phonon density of states. The IFCs embedding procedure [58, 59] was employed with a cut-off radius $R_c=5.7$ Å. Three high-coupling modes are displayed at the bottom of this figure. The total HR factor is small ($S \approx 2.15$), indicating a weak coupling regime, for which apparent vibronic progression are expected. The HR spectral function is shaped by a broad feature from around 20 meV to 60 meV, where most of the coupling comes from pristine delocalized modes or pseudo-local modes (see (ii) mode on figure 6.16). Just below 20 meV, a sharp peak is the signature of the coupling with Eu-based local modes. At 100 meV, another sharp peak is observed and corresponds to the coupling with

below-gap local modes involving the O, Si, and N atoms within the first and second shell environment of the Eu atom. A visual inspection of this mode reveals that the pattern of displacements vaguely resemble an asymmetric breathing mode of the Eu-N₉ polyhedron.

6.3.4 Photo-luminescence lineshape

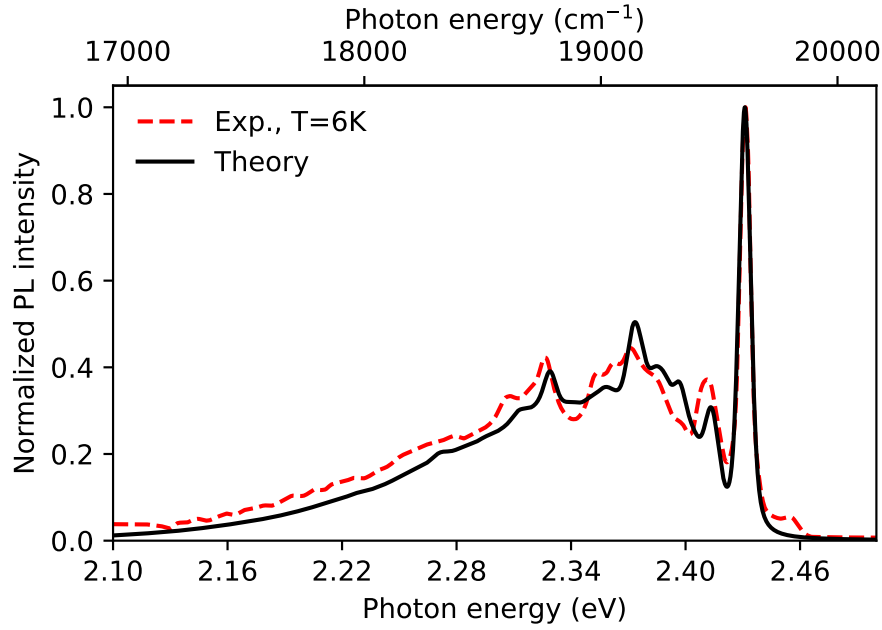


Figure 6.17: Experimental [180] and theoretical PL spectrum of low- z β -SiAlON:Eu²⁺ at T=6K where a shift of 0.24 eV was applied to match the zero-phonon lines.

The PL lineshape is computed based on the Huang-Rhys spectral function presented in the previous section and compared to experimental data at T=6K, see figure 6.17. The ZPL energies are aligned in order to compare the vibronic progression. The agreement is excellent and constitutes a major result of this PhD thesis. One can comment on the physical origin of the three main phonon features appearing in the PL spectrum. Starting from the ZPL line, the first phonon peak at ≈ 2.41 eV is the one-phonon contribution of the localized Eu-based mode. The next broad peak comes from bulk-like delocalized Si-N modes. The last peak at ≈ 2.33 eV is the signature of the one-phonon contribution

of the pseudo-breathing mode of the Eu environment, as described in the previous section.

6.3.5 *Discussion on the Eu location and perspectives*

Based on the excellent agreement between the PL lineshape obtained from the model structure presented on figure 6.12 and the experimental PL lineshape, one might conclude that the debate is settled; the model structure is the correct *real-life* structure. Such a statement might be premature and one has to be cautious. Indeed, while these results confirm that such a model structure causes the experimental lineshape, it might be that other structural models, not tested here, could also provide this lineshape.

One might first test the model structure with a Eu-N₁₂ environment with a similar methodology to see if the observed experimental lineshape could be a statistical mix of Eu atoms in different Nitrogen environments. Varying the positions of the O and Al atoms in the 225-atom supercell might be interesting, to observe if their positions play a role. It is hypothesized that the Eu location along the channel is more important than the exact distribution of O and Al atoms around the Eu interstitial. Indeed, the analysis of the HR spectral function revealed no significant role of the O/Al atoms in shaping the PL lineshape. One might finally try to explain the red-shift of luminescence with increasing *z* value by incorporating more Al/O substitutions in the 225-atom supercell, and observe the change in ZPL energy. All these improvements might be the subject of future investigations.

6.4 THE PUZZLING CASE OF CaO:Eu^{2+}

This section presents an account of the computational studies conducted on CaO:Eu^{2+} . These studies were carried out as this phosphor present clear vibronic peaks at low-T. While similar methodologies were successfully applied to other phosphor materials, the application to CaO:Eu^{2+} resulted in significant challenges. In particular, issues surrounding symmetry breaking, metastable states, and discrepancies between calculated and experimental photoluminescence spectra are discussed.

Symmetry Breaking and Relaxation in the Excited State

Initial calculations using a modest 54-atom supercell we performed by constraining the system to adopt high symmetry. The Eu atom is coordinated by six oxygen in a perfect octahedron in both ground (Eu-O distance $\approx 2.5\text{\AA}$) and excited state (Eu-O distance $\approx 2.43\text{\AA}$). It showed intriguing excited state band structure presented on figure 6.18, left. Instead of having a single "traditional" 4f hole located in the gap, three nearly-degenerate bands are observed in the gap, close the VBM. These three 4f states showed pronounced hybridization with oxygen 2p states. Three t_{2g} 5d states are degenerate. The computed ZPL is 2.80 eV, far from the experimental ZPL (≈ 1.77 eV). Such discrepancy led to a series of trials to reconcile theory and experiment.

The use of fractionnal occupancies on the highest occupied states was first tested, no significant change was observed. The effects of symmetry breaking was explored. First, a small random perturbation (0.02 $\text{\AA}$) was introduced to all atoms in the supercell before relaxation. This resulted in a notable stabilization of the excited state due to a Jahn-Teller distortion, reducing the energy by approximately 1 eV compared to the fully symmetric configuration. In addition, the electronic band structure presents now a single 4f hole and a very small lifting of the 5d three-fold degeneracy. We obtain in such case $E_{\text{ZPL}} = 1.45\text{eV}$. This distortion in the excited state suggests that symmetry breaking plays a significant role in stabilizing the system, yet it introduces additional challenges in terms of convergence due to multiple possible metastable configurations.

Different slight initial "kicks" were given before relaxing in the excited state, in order to lower the symmetry. The results are summarized in table 6.1. In this table, the deformation of the first six columns refers

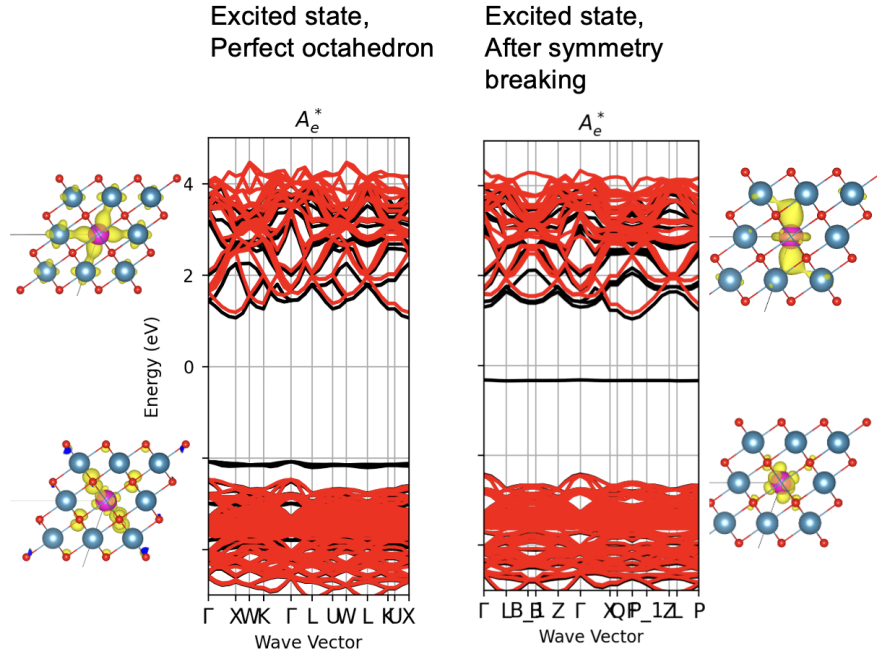


Figure 6.18: Change in the excited state Kohn-Sham electronic band structure when breaking the symmetries in CaO:Eu^{2+} .

to the change in atomic positions (in Å) before relaxation. For instance, (0.0, 0.0, 0.2) means that the two atoms at the top of the octahedron are stretched along z (initial elongation of the octahedron). The two last columns refers to a 111 and 110 plane extensions. In each case, the initial deformation led to a lowering of the energy. However, the final energy state was found to depend strongly on the initial configuration, resulting in different metastable solutions.

PL Spectrum

Among the numerous available states, the lowest in energy was selected to perform a full multi-phonon mode Huang-Rhys analysis. The computed Huang-Rhys spectral function is shown on figure 6.19, with the projected phonon DOS of bulk CaO. Two strong peaks around 60 meV are distinguished and result from a large coupling with pseudo-local "breathing" modes. These modes couples indeed strongly with the 5d-4f forces also presented in this figure. The total computed Huang-Rhys factor is large ($S \approx 10$). With such high coupling, the computed

Defo.	E_{zpl} (eV)	ΔR (Å)	Relative Energy (eV)
(0.0, 0.0, 0.0)	2.376632	0.216621	0.0000
(0.02, 0.0, 0.0)	1.314397	0.290115	-1.0616
(0.0, 0.02, 0.0)	2.137919	0.247480	-0.2387
(0.0, 0.0, 0.02)	1.323867	0.289701	-1.0529
(-0.01, -0.01, 0.01)	1.323860	0.291190	-1.0528
(-0.015, 0.015, -0.005)	1.323874	0.289595	-1.0528
(1, 1, 1)	1.094693	0.289885	-1.2819
(1, 1, 0)	1.107269	0.290869	-1.2694

Table 6.1: Initial deformation, E_{zpl} , ΔR (Å), and relative energies for various meta-stable states obtained after different initial conditions.

lineshape presents a gaussian shape, even at low temperature, in total contradiction with experiment (figure 6.20, left). In order to check if the 5d-4f forces were not strongly overestimated, we have scaled these forces to check if the vibronic peaks were at least correctly placed, as in the case of $\text{SrCl}_2:\text{Eu}^{2+}$. The result is shown on figure 6.20, middle. By dividing the forces by two, the experiment is not recovered. This means that the problem appears to be more severe than in the case of $\text{SrCl}_2:\text{Eu}^{2+}$. Physics seems to be missing. A Huang-Rhys fitting with three phonon modes was performed and allows one to obtain a reasonable agreement with experiment, as shown on figure 6.20, right. It suggests that the target should be to obtain three distinct peaks in the Huang-Rhys spectral function at 27, 46, and 63 meV, with similar contributions, and a total $S \approx 3$.

Finally, to investigate potential interactions between Eu ions, supercells containing two Eu atoms placed in different configurations were constructed. The calculations indicated that the formation of an Eu_2 dimer was energetically favorable compared to the isolated Eu ion configuration.

Potential issues

In short, the observed discrepancies are still a mystery at the time of writing. This is at the same time interesting and frustrating. Interesting because this means that the model used reaches its limit for this system. Understanding these limitations is always a beneficial step forward for

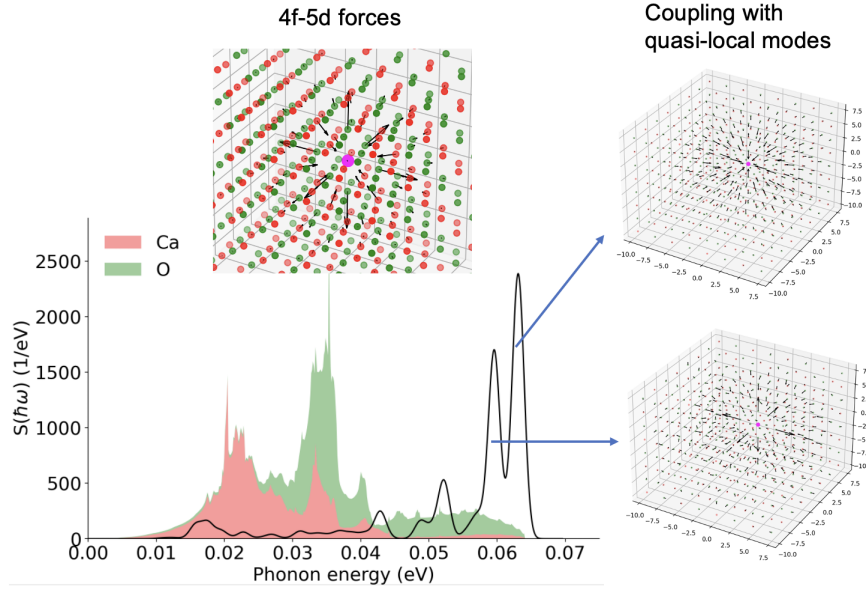


Figure 6.19: Computed Huang-Rhys spectral function in CaO:Eu^{2+} .

a better control of the method. This is also frustrating because it is not clear which part(s) of the model is responsible for the discrepancy. Here is a list of observations that might hopefully help a future investigation of this system :

- 1) **INCORRECT SYSTEM ASSUMPTION** The simulated system may not accurately represent the real material. Oxygen vacancies were recently identified to act as optical center killers in CaO:Eu^{2+} and are energetically favored [182]. The current model assumes a perfect crystal with Ca:Eu substitution, potentially missing the role of nearby oxygen vacancies. It would suggest that the total PL spectrum is formed by Eu atoms in Eu-O_5 environment only, in order to obtain the experimentally observed small inhomogeneous broadening.
- 2) **PHONON METHODOLOGY** The methodology related to phonon calculations, Huang-Rhys factors, and embedding seems robust and does not appear to be the source of the problem.
- 3) **JAHN-TELLER STABILIZATION** If the optical center involves the Eu-O_6 environment, Jahn-Teller stabilization could play an important role. But one might find multiple metastable states with strong depend-

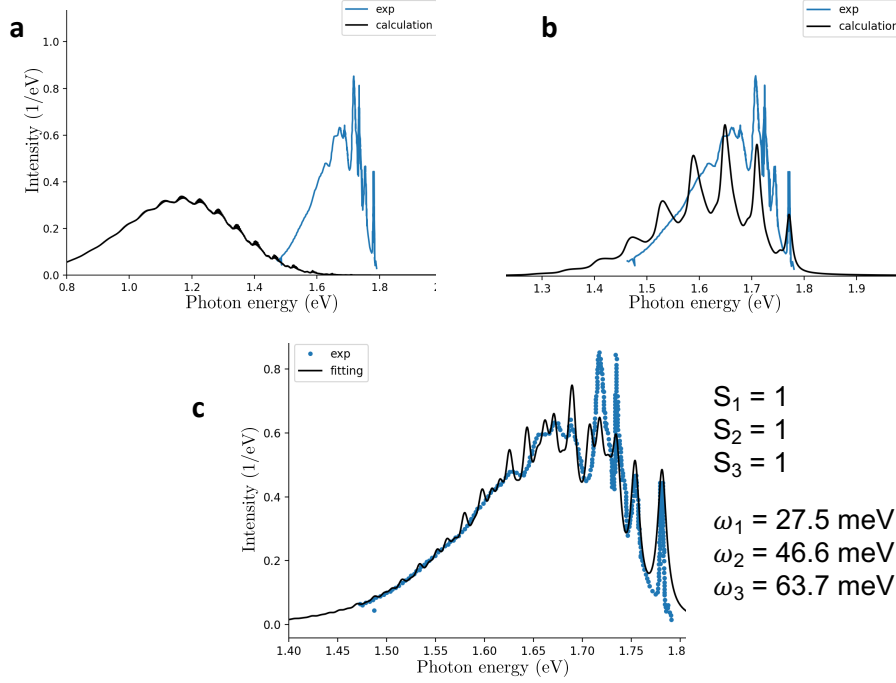


Figure 6.20: **a** : Computed lineshape of CaO:Eu²⁺. **(b)** Computed lineshape after dividing the forces by two. **(c)** Fitting of the experiment with a three-modes model.

ence on the initial structure. It is also noted that a very recent work quantified the effect of Jahn-Teller interactions in optical lineshapes observed in systems characterized by strong Jahn-Teller interactions [183]. Looking into the methodology used in this study might be fruitful.

4) TREATMENT OF THE EXCITED STATE One might go beyond the Δ SCF method with PBE+U on the 4f states of Eu. The use of hybrid functional would be interesting, although it is not clear at the time of writing if f electrons are handled properly with hybrids. One could also try to rely on a different treatment of the excited state : it is indeed recognized that the Δ SCF works well if the excited state is well approximated by a single Slater determinant and might be the subject of numerical convergence issues for (near-)degenerate excited states [184].

It is noted that the transition energies of excited states presenting multi-determinant nature can be computed by combining energies from

several single-determinant calculations, following the recent approach proposed by Van de Walle et al. [185, 186].

More accurate approaches based on quantum embedding theories [187–191] could also be relevant here. In such approaches, an active space representing the manifold of defect states is identified, and these states are treated at a higher level of theory (for instance full CI, GW,...) than the electronic structure of the rest of the host crystal (for instance DFT).

6.5 CONCLUSION OF THE RESULTS

Let us recap this rather lengthy chapter by focusing on the results obtained for $\text{SrCl}_2:\text{Eu}^{2+}$, $\text{CaSO}_4:\text{Eu}^{2+}$, and $\beta\text{-SiAlON}:\text{Eu}^{2+}$. A conclusion specific to the UCr_4C_4 compounds can be found in Section 5.5.

The vibronic processes occurring in the $\text{SrCl}_2:\text{Eu}^{2+}$ and $\text{CaSO}_4:\text{Eu}^{2+}$ phosphors have been characterized from first principles. In the structurally simpler $\text{SrCl}_2:\text{Eu}^{2+}$, the Eu-Cl_8 cube shrinks isotropically upon absorption, and this isotropic atomic relaxation extends beyond the first coordination shell into many unit cells. By comparing the use of forces and displacements in determining the Huang-Rhys factor, we have highlighted potential anharmonic behavior in this system. The overestimation of the Huang-Rhys factor when using forces was also observed by comparing the theoretical spectrum with experimental data. A good agreement was recovered by scaling the forces.

In $\text{CaSO}_4:\text{Eu}^{2+}$, the situation is more complex due to anisotropy: the Eu-O_8 polyhedron shrinks and distorts upon absorption, and specific displacement patterns are observed along different directions (a similar situation is observed in other "complex" structures). In this system, the harmonic approximation is well justified, and the computed lineshape agrees well with experiment. The multi-phonon modes Huang-Rhys model, combined with the computation of defect phonons in large supercells, enabled the identification of both delocalized and localized modes that couple with the electronic transition.

These two examples permitted to illustrate the predictive power of the methodology developed in this PhD work. A further step was taken by applying this method to shed new light on the precise identification of luminescent centers in the technologically important $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ red phosphor and the low- z $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}:\text{Eu}^{2+}$ green phosphor.

In $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ (detailed in the previous chapter), two Sr sites can host the Eu atom, and two distinct spectra can be experimentally

distinguished. We simulated the luminescence spectra originating from both luminescent sites and, through comparison with experimental data, assigned them to their specific microscopic environments, answering the key question: "Which spectrum corresponds to which site?". We also quantified the effect of thermal expansion on the luminescence shift in this material.

In $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}:\text{Eu}^{2+}$, numerous experimental and theoretical studies have sought to understand the link between the microscopic environment surrounding the Eu interstitial and the luminescent properties. Here, we simulated the luminescence spectra from a model structure with defined Eu-Al-O positions in the host lattice and found excellent agreement with experimental results, confirming the adequacy of this model in explaining the luminescent properties of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}:\text{Eu}^{2+}$.

Finally, the investigation of $\text{CaO}:\text{Eu}^{2+}$ underscores challenges associated with the applied methodology. Despite initial successes in the calculation of vibronic spectra, the persistent discrepancy between theory and experiment indicates inherent limitations in the current model. Notably, issues related to symmetry breaking, Jahn-Teller distortions, and the potential multi-determinant nature of the excited states have been identified. The unresolved discrepancies offer important insights into the boundaries of the existing theoretical frameworks and highlight areas for future development in accurately modeling phosphor systems.

CONCLUSION

The luminescent properties of phosphor materials are essential for modern lighting technologies, as they are key components of phosphor-converted white LEDs. This thesis has contributed to both the fundamental understanding and practical modeling of these properties. By employing first-principles simulations, we have advanced the study of vibronic processes governing the shape of the emission spectrum in Eu-doped phosphors.

In chapters 1 and 2, we established the theoretical framework for efficiently computing the luminescence spectrum originating from defect centers in solids. This included a detailed description of the Huang-Rhys model, incorporating both the simple effective phonon-mode approach and the more realistic multi-phonon mode model, alongside the efficient generating function formalism.

Density functional theory (DFT) was used throughout this work to derive the necessary parameters—such as the zero-phonon line energy, atomic displacements, forces induced by radiative electronic transitions, and phonon modes. Chapter 3 outlines how these components can be obtained in practice using DFT. We critically assessed the constrained-occupation Δ SCF method used in this work to simulate the excited state, highlighting both its benefits (such as relatively low computational cost, ease of use, and ability to relax structures in the excited state) and its limitations (less theoretical rigor compared to more computationally expensive methods like Bethe-Salpeter formalism or wave-function-based methods, potential convergence issues, and difficulties in handling near-degenerate excited states or excited states that are poorly approximated by a single Slater determinant).

Early in this PhD project, with the initial study of $\text{SrLi}_2\text{Al}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$, it became apparent that the finite size of supercells, typically containing a few hundred atoms, could cause non-negligible error cancellations in systems with long-range atomic displacements. Additionally, describing the coupling with long-wavelength phonons was critical but challenging, as achieving this “dilute” limit typically requires supercells containing thousands of atoms. Therefore, we employed dedicated techniques to compute the Huang-Rhys spectral function in large supercells

containing the defect. This included using forces instead of displacements and an embedding procedure on the matrix of interatomic force constants, which allowed us to compute phonon modes for large supercells while preserving local defect phonons. This approach enabled us to obtain Huang-Rhys spectral functions shaped by both bulk-like delocalized modes and highly localized defect modes, representing a step forward in the realistic description of vibronic processes.

The development of the Lumabi computational tool is a significant achievement of this thesis, described in chapter 4. It automates key steps in determining the luminescence lineshape: from the initial Δ SCF DFT calculations, to generating defect phonon modes in large supercells with the interatomic force constant (IFC) embedding procedure, and ultimately to generating photoluminescence (PL) spectra based on Huang-Rhys theory and the efficient time-domain generating function approach. This tool was extensively developed and used throughout this PhD, and it is hoped that Lumabi will enable other researchers to perform similar simulations more efficiently in the future.

Coming now to the application of the methodology on phosphor materials, we first discussed UCr_4C_4 -type phosphors in chapter 5. A common atomic displacement pattern was observed across these structures: upon electronic excitation, the Eu-centered first coordination shell shrinks, and long-range relaxations of Sr-Ca atoms along the cation channels occur. This second pattern plays a critical role in shaping the emission spectrum of these materials. Specifically, the narrow FWHM of the luminescence spectra in UCr_4C_4 -type phosphors can be attributed to the combination of a small normal coordinate change, ΔQ , and a small effective coupling frequency, ω_{eff} . These factors are linked to the rigidity of the UCr_4C_4 structure and the coupling between long-range displacements and low-frequency phonon modes.

We then examined in chapter 6 the interesting case of $\text{SrCl}_2\text{:Eu}^{2+}$, where anharmonic behavior was identified. The computed Huang-Rhys factor had to be corrected by scaling the forces to match experimental results. In contrast, for the more complex $\text{CaSO}_4\text{:Eu}^{2+}$ system, the harmonic approximation was sufficient to model the luminescence lineshape, achieving excellent agreement with experimental data.

Furthermore, the methodology developed in this thesis was used as a tool to identify defect centers responsible for luminescence through their vibronic fingerprint. In $\text{SrLiAl}_3\text{N}_4\text{:Eu}^{2+}$ (belonging to the UCr_4C_4 family and hence described in chapter 5), the two non-equivalent Sr sites were distinguished based on their respective luminescence spectra.

By comparing experimental data with simulated spectra for both Sr sites, we were able to assign each spectrum to a specific microscopic environment. Additionally, the thermal expansion effect on the luminescence blue shift was successfully modeled and quantified, further enhancing our understanding of this material's behavior at different temperatures.

In β -SiAlON:Eu²⁺, a widely studied green-emitting phosphor with both technological and theoretical relevance, the precise location of the Eu atom and Al/O substitutions had not been settled. The simulations accurately captured the experimental vibronic peaks using a model structure from a previous study, offering strong validation of the structural model.

Before concluding, it is important to address the limitations and challenges encountered in this work, as well as to propose potential future research directions.

First, a deeper understanding of the potential failures of the constrained-occupation Δ SCF method would be valuable. In which situations does it fail, and why? CaO:Eu²⁺ comes to mind as an example. Indeed, in this system, the reason for the observed discrepancies between simulation and experiment are not currently known. Potential issues includes an incorrect guess structure (role of oxygen vacancies), a Jahn-Teller stabilisation effect, or the inadequate use of the Δ SCF method for near-degenerate states. In order to understand the luminescence in this system, it might be beneficial to make comparisons with higher-level theories, such as wave-function-based methods or embedding theories, which are more computationally demanding. At present, it is not easy to know *a priori* when the Δ SCF method will not correctly describe the excited state of a given system. Convergence difficulties are often encountered, which were often resolved on a case-by-case basis. The current status is that the success of this methodology remains too material-dependent to be fully automated for large-scale screening of hundreds of thousands of defect systems, each with distinct excited state properties, to identify optimal phosphor candidates.

It is also well known that classical DFT, as used in this work, tends to underestimate band gaps. While this is not problematic for large-gap compounds, where defect states (such as Eu_{5d} and Eu_{4f} in this work) are well accommodated in the gap, it becomes an issue for systems with small band gaps. This underestimation creates a gap too small to accommodate defect states correctly, which is why no results were reported for another interesting UC₄C₄-type phosphor, Sr[Mg₃SiN₄]:Eu²⁺. Future

work could explore the use of hybrid functionals for lanthanide-based phosphors, as this is now the state of the art for simple defect systems like the NV center in diamond. However, the treatment of f electrons with hybrid functionals remains an open question.

Throughout this work, the harmonic approximation was used implicitly in many places. However, anharmonic behavior has been shown to occur in certain systems, such as $\text{SrCl}_2:\text{Eu}^{2+}$. Exploring the impact of anharmonicities on luminescent properties would be an interesting avenue for future research.

Regarding the family of UCr_4C_4 phosphors, we studied compounds in which the Eu atom substitutes divalent cations (Ca, Sr, Ba). Recent experimental studies have demonstrated the promising performance of UCr_4C_4 oxide phosphors with monovalent cations (Na, K, Rb), while still maintaining the same one-dimensional cation channels. Applying the methods used in this thesis to these compounds could yield further insights.

Finally, beyond the technical advances presented in this thesis, it is important to consider the broader implications of phosphor-converted white LEDs in the context of energy efficiency and environmental sustainability. LEDs have revolutionized lighting technology by significantly reducing energy consumption compared to traditional incandescent and fluorescent lighting. This efficiency translates directly into lower greenhouse gas emissions, contributing to global efforts to mitigate climate change. Moreover, the development of high-performance phosphors plays a critical role in improving LED efficacy, color rendering, and longevity, further enhancing their sustainability. However, challenges remain, such as the environmental impact of rare-earth mining and the monopoly of a few countries over the supply of lanthanides, which raises concerns about resource availability and geopolitical dependencies. This highlights the need for further research on alternative luminescent materials that do not rely on rare-earth elements, as well as the development of eco-friendly synthesis methods and circular economy strategies to minimize the ecological footprint of LED technologies.

Appendices

A

COMPUTATIONAL SETTINGS AND ADDITIONAL RESULTS

This appendix aims at gathering the computational parameters used throughout this work. It starts with the common settings used to obtain the results on the seven phosphors materials presented in the chapter 5. Material-specific sections then include material-specific parameters and potential additional results and figures not shown in the main body of this manuscript.

A.1 COMMON COMPUTATIONAL METHOD

Calculations are performed with density-functional theory using the ABINIT software [128, 192]. Core electrons are treated with the PAW method, with JTH atomic data [193, 194]. The generalized gradient approximation (GGA-PBE) is used to treat exchange-correlation effects [195] and a Hubbard $U=7$ eV term is added on the $4f$ states of europium, consistently with previous works [77]. Calculations on europium-doped materials are conducted using the supercell technique with supercell sizes of a few hundred of atoms. The largest supercell sizes used in this work are collected on table A.1 for each material studied. When multiple possible emission centers exists, they are treated as independent calculations. For these defect structures, the structures are relaxed below a maximal residual force of 10^{-4} Hartree/Bohr. The cut-off kinetic energy is 25 Ha with a single zone centered $\mathbf{k}$ -point. For the treatment of the Eu $4f^65d^1$ excited state, the Δ SCF method is used whereby the eigenfunctions associated to the highest predominantly Eu $4f$ band are forced to be unoccupied while the next predominantly Eu $5d$ energy band is constrained to be occupied. Although spin-orbit coupling can present a noticeable effect on the excited state electronic configuration, it is not considered here due to its small effect on the

emission spectra [77]. This work focuses on the lowest excited state of the $4f^65d^1$ multiplet (7F_J , $J = 0-6$) splitting and does not try to account for the other states. The phonons modes of the pristine materials are computed in ABINIT with DFPT [114, 196]. The coarse q-grids of each material studied are collected in table A.1. The phonons modes of the defect structures are computed on the same supercell than the Δ SCF structure computation with the finite-displacements method as implemented in Phonopy [109, 148]. For the embedding of the interatomic force constants described in chapter 3, the largest cut-off radii R_c used for each material is reported on table A.1.

We now provide the typical orders of magnitude for the computational cost of these calculations. In the following, CPU will refer to single-core CPU. For a single system with approximately 200 atoms, DFT atomic relaxation can require anywhere from 1000 to 10 000 CPU hours, depending on the starting configuration and convergence behavior. The cost of a pristine cell DFPT calculation varies significantly with the unit cell size and the q-point grid density, ranging from around 100 CPU hours for small systems to 1000–10 000 CPU hours for larger systems with minimal symmetry. The most computationally demanding step is the finite difference calculation of the doped system to obtain defect phonons. This process may involve around 500 static calculations, each requiring 100–1000 CPU hours, particularly if convergence is slow.

A.2 SALON:EU²⁺

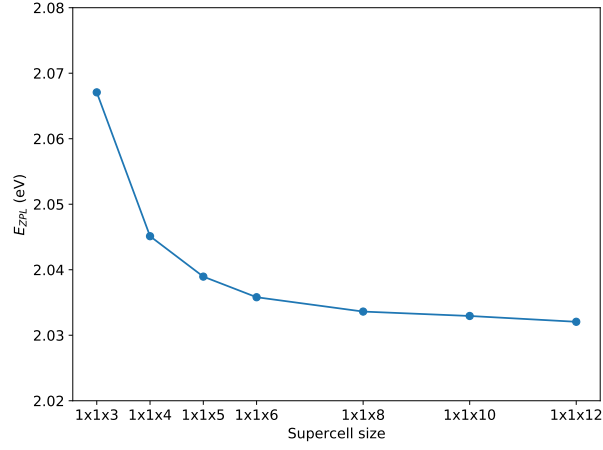


Figure A.1: Convergence of the zero-phonon line energy E_{ZPL} as a function of the supercell size. As opposed to the structural relaxation parameters, the values associated to small sizes are already reasonably good.

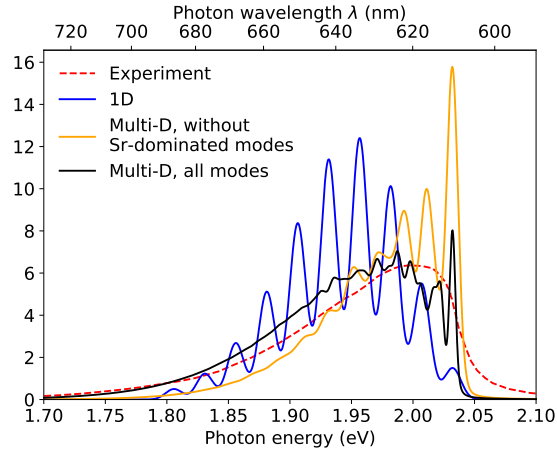


Figure A.2: Comparison of normalized luminescence intensity $L(\hbar\omega)$ with a small smearing and without shift of E_{ZPL} . Blue line: 1D model, with a single effective mode. Orange: multi-dimensional model, where the Sr-dominated modes were excluded. Black line: multi-dimensional model, with a full phonon decomposition. We notice how the multi-D model reproduce well the long tail of the experimental spectrum.

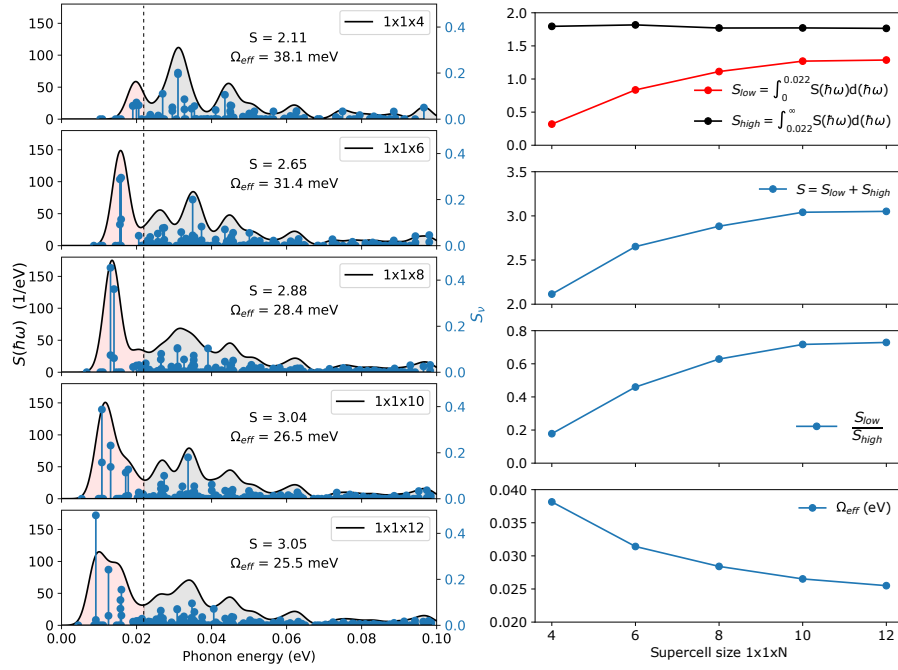


Figure A.3: Convergence of the spectral function $S(\hbar\omega)$ as a function of the supercell size. Integrated contribution from high-energy phonons (threshold fixed at 22 meV) is nearly constant with the supercell size while integrated contribution from low-energy phonons slowly converges. Their sum and their ratio is nearly converged for a $1 \times 1 \times 12$ supercell. On the other hand, the exact shape of the low-energy part is still not obtained. This issue is due to the coupling to long-wavelength acoustic modes

Compound	Unit cell	Supercell size	DFPT coarse $\mathbf{q}$ -grid	IFC emb. cut-off R_c
$\text{CaLiAl}_3\text{N}_4:\text{Eu}^{2+}$	tetragonal ($I4_1/a$) 144 atoms $a=b=11.245\text{\AA}$ $c=12.995\text{\AA}$	$[1,1,1]$ 144 atoms	$[2,2,2]$	/
$\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$	triclinic ($P-1$) 36 atoms $a=5.88\text{\AA}$, $b=7.53\text{\AA}$, $c=9.99\text{\AA}$ $\alpha=83.58^\circ$, $\beta=76.82^\circ$, $\gamma=79.55^\circ$	$[2,2,2]$ 288 atoms	$[2,2,2]$	$5.5\text{\AA}$
$\text{SrLi}_2\text{Al}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$	tetragonal ($P4_2/m$) 18 atoms $a=b=8.02\text{\AA}$, $c=3.20\text{\AA}$	$[1,1,12]$ 216 atoms	$[4,4,4]$	/
$\text{SrLi}_3\text{AlO}_4:\text{Eu}^{2+}$	triclinic ($P-1$) 36 atoms $a=5.75\text{\AA}$, $b=7.33\text{\AA}$, $c=9.72\text{\AA}$ $\alpha=83.88^\circ$, $\beta=76.59^\circ$, $\gamma=79.57^\circ$	$[2,2,1]$ 144 atoms	/	/
$\text{SrCl}_2:\text{Eu}^{2+}$	cubic ($Fm-3m$) 3 atoms $a=b=c=4.983\text{\AA}$ $\alpha=\beta=\gamma=60^\circ$	$[4,4,4]$ 192 atoms	$[8,8,8]$	$7.4\text{\AA}$
$\text{CaSO}_4:\text{Eu}^{2+}$	orthorhombic ($Cmcm$) 12 atoms $a=b=4.75\text{\AA}$ $c=7.10\text{\AA}$ $\alpha=\beta=90^\circ$, $\gamma=96.98^\circ$	$[3,3,2]$ 216 atoms	$[6,6,6]$	$6\text{\AA}$
$\beta\text{-SiAlON}:\text{Eu}^{2+}$	hexagonal ($P6_3/m$) 14 atoms $a=b=7.64\text{\AA}$ $c=2.92\text{\AA}$	$[2,2,4]$ 225 atoms	$[5,5,10]$	$5.7\text{\AA}$

Table A.1: For each phosphor studied in this work: structural informations about the pristine unit cell, the supercell size used in the defect calculations, the DFPT coarse $\mathbf{q}$ -grid used to compute the pristine phonons and the cut-off radii R_c used in the IFC embedding method. Missing informations for the coarse $\mathbf{q}$ -grid indicates that the phonons were not computed for the compound. Missing information for the cut-off radii R_c indicates that the defect phonon were not computed.

A.3 SLA:Eu²⁺

Huang-Rhys spectral function convergence

Phonons modes of the undoped primitive cell of SLA containing 36 atoms are obtained by diagonalizing the dynamical matrices computed with DFPT with a $2 \times 2 \times 2$ $\mathbf{k}$ -points and $\mathbf{q}$ -points grids and then Fourier interpolated on a fine $4 \times 4 \times 4$ $\mathbf{q}$ -grid [114].

The IFCs of the pristine SLA, computed on a $4 \times 4 \times 4$ $\mathbf{q}$ -grid, are mapped on the corresponding $4 \times 4 \times 4$ supercell. The IFCs of the Eu-doped system are computed on a smaller $2 \times 2 \times 2$ supercell containing 288 atoms using a frozen phonon approach as implemented in the PHONOPY package [148]. We have performed in figure A.4 a convergence study of the Huang-Rhys spectral function as a function of the size of the large supercell. The result is shown in A.4 with $2 \times 2 \times 2$, $4 \times 2 \times 2$, $3 \times 3 \times 3$, $4 \times 4 \times 2$, $4 \times 4 \times 4$ supercells containing respectively 288, 576, 972, 1152 and 2304 atoms. The cut-off R_c is set to $5.5 \text{ \AA}$. We have also tried a cut-off off $5 \text{ \AA}$. The total Huang-Rhys factors of both sites change by less than 1% with no noticeable change on the shape of the spectral function.

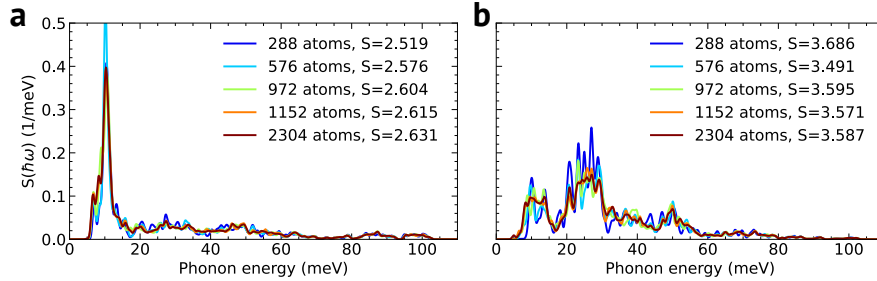


Figure A.4: Convergence of the Huang-Rhys spectral function as a function of the size of the large supercell $2 \times 2 \times 2$, $4 \times 2 \times 2$, $3 \times 3 \times 3$, $4 \times 4 \times 2$ and $4 \times 4 \times 4$, for **a** site 1 and **b** site 2.

Thermal expansion

To compute the effect of thermal expansion, the quasiharmonic approximation (QHA) is used neglecting deviatoric thermal stresses and internal forces [197–199]. The only contribution to thermal expansion of the crystal is due to the coupling between phonons and the change

in unit cell volume [200], with cell parameters and internal coordinates relaxed at fixed volumes. We obtain the temperature versus volume curve of the undoped SLA by minimizing the Helmholtz free energy (FE) [162, 163, 201]:

$$F(V, T) = E(V) + F^{\text{vib}}(V, T), \quad (\text{A.1})$$

where

$$F^{\text{vib}}(V, T) = \sum_{q\nu} \frac{\hbar\omega_{q\nu}(V)}{2} + k_{\text{B}}T \ln(1 - e^{-\frac{\hbar\omega_{q\nu}(V)}{k_{\text{B}}T}}), \quad (\text{A.2})$$

where $E(V)$ is the static DFT energy versus volume curve, with all non-volumic degrees of freedom relaxed, and $F^{\text{vib}}(V, T)$ is the vibration energy with the same cell and atomic geometry. The FE curve is constructed using seven configurations within a $[-2\%, +4\%]$ volume change with respect to the static equilibrium volume. The minimum volume for a given temperature is obtained by fitting a Murnaghan equation of state [202] to the FE curve. For each volume, we relaxed the structure with constrained volume and we computed the phonon density-of-states with DFPT using a $2 \times 2 \times 2$ $\mathbf{k}$ -point and $\mathbf{q}$ -point grid and Fourier-interpolated it to a $15 \times 15 \times 15$ fine $\mathbf{q}$ -grid. The minimum volume for a given T (red dots) is obtained using Murnaghan equation of state for the fitting (blue curves). The DFT static curve is displayed in black. This allows to extract the zero-point volume (ZPV) which is computed to be an increase of 0.9% between the minimum volume of the DFT static curve and the minimum volume of the Helmholtz free energy at 0 K. The volume dilation with temperature is shown in figure A.5b, from which we extract the temperature-dependent volumic thermal expansion coefficient ($\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T}$) shown in figure A.5c.

We assessed the impact of thermal expansion on ZPL energies by scaling the lattice parameters of the bulk unit-cell SLA to the 288 atom supercells. We then performed the complete Δ SCF procedure at fixed volumes corresponding to selected temperatures (10 K, 100 K, 200 K, 293 K, 373 K, 473 K, 573 K). This method enabled us to evaluate the temperature-dependent shift of the ZPL energies and the zero-point volume effect on the ZPL energy at 0 K. The ZPL vs volume curve is shown on figure A.6 while the corresponding ZPL vs T curve is shown in the figure 5.10 of the main text. A linear relationship is found for both sites with a slope of 0.66 meV/ $\text{\AA}^3$ for site 1 and 0.72 meV/ $\text{\AA}^3$ for site 2

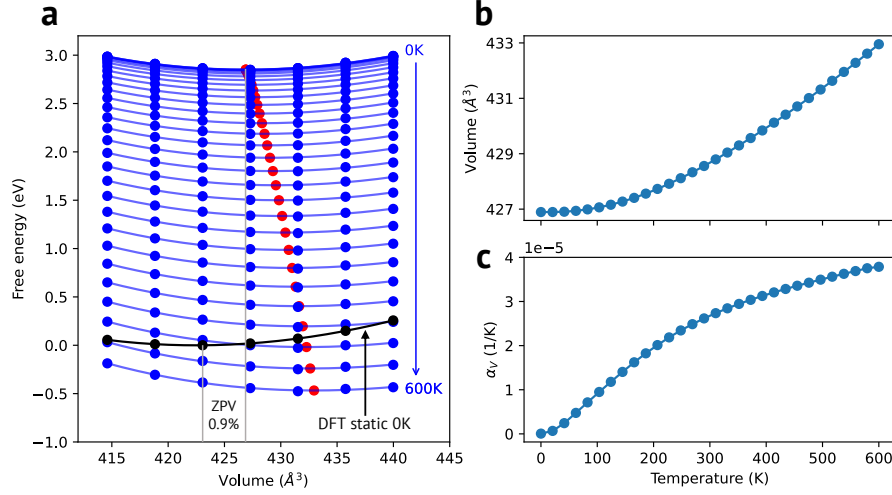


Figure A.5: **a** Helmholtz free energy as a function of volume from 0 K to 600 K, using seven configurations within a $[-2\%, +4\%]$ volume change with respect to the static undoped unit-cell equilibrium volume. The minimum volume for a given T (red dots) is obtained using the Murnaghan equation of state. The DFT static curve is displayed in black. A zero-point volume (ZPV) of 0.9% is computed. **b** Change of volume with temperature and **c** change of volumic thermal expansion coefficient ($\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T}$) with temperature.

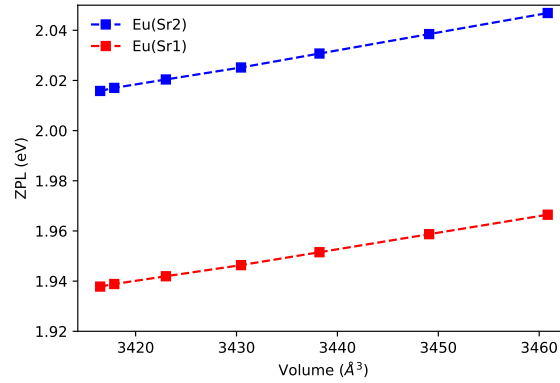


Figure A.6: Change of zero-phonon line (ZPL) with volume where the different volumes are those corresponding to the selected temperatures. A linear relationship is found for both sites with a slope of $0.66 \text{ meV}/\text{\AA}^3$ for site 1 and $0.72 \text{ meV}/\text{\AA}^3$ for site 2.

Structural parameters

The table A.2 compares the relaxed cell parameters as computed in this work for bulk SLA with the experimental results [28]. We find an overestimation of the structural parameters by about 0.3%, which is common for PBE exchange and correlation functional. The angles match within 0.05°. Tables A.3 and A.4 show the local structural parameters around Sr1 and Sr2 in the pristine structure, as well as when replaced by Eu in the 4f ground or 5d excited state. In the pristine SLA, we first observe that within the Sr chain, the Sr1-Sr1 distance of 3.2 Å is shorter than the Sr2-Sr2 distance of 3.42 Å. The Sr1-Sr2 distance is in between, with a value of 3.28 Å. The mean distance between the Sr atom and its eight N neighbors is very similar in both sites (2.809 Å and 2.804 Å). When the Sr atoms are replaced by Eu atom, these distances change by less than 0.1% due to similar atomic radii of the Eu^{2+} and Sr^{2+} atoms [151]. When going from the 4f ground state to the 5d excited state, the mean Eu-N₈ shrinks in both sites by 1.32% and 1.35%, respectively. Regarding the Sr chain, their atomic distances Eu(Sr1)-Sr1 and Eu(Sr1)-Sr2 decrease by 1% and 1.3%, respectively. In the case of Eu(Sr2) instead, the distances elongate by 1.2% and 0.3%, respectively.

	Exp. [28]	This work
a [Å]	5.866	5.883
b [Å]	7.511	7.532
c [Å]	9.965	9.995
α [°]	83.603	83.656
β [°]	76.772	76.837
γ [°]	79.565	79.596
Cell volume [Å ³]	419.250	423.047

Table A.2: Cell parameters of the undoped SLA as computed in this work compared to experimental results [28].

	pristine (X=Sr1)	X=Eu(Sr1)-4f	X=Eu(Sr1)-5d
X-Sr1 distance [$\text{\AA}$]	3.202	3.205	3.174
X-Sr2 distance [$\text{\AA}$]	3.278	3.277	3.234
Mean X-N distance [$\text{\AA}$]	2.809	2.813	2.776

Table A.3: Local distances around the Sr1 atom in the pristine structure, or when replaced by an Eu atom in the 4f or 5d electronic state.

	pristine (X=Sr2)	X=Eu(Sr2)-4f	X=Eu(Sr2)-5d
X-Sr1 distance [$\text{\AA}$]	3.278	3.280	3.319
X-Sr2 distance [$\text{\AA}$]	3.424	3.423	3.433
Mean X-N distance [$\text{\AA}$]	2.804	2.806	2.768

Table A.4: Local distances around Sr2 atom in the pristine structure, or when replaced by Eu atom in the 4f or 5d electronic state.

Kohn Sham levels

In figure A.7, we compare the localized DFT eigenstates at the zone center for the $2 \times 2 \times 2$ supercell where one atom of Sr has been replaced by an Eu in the two inequivalent positions. We observe a character inversion of the lowest two 5d conduction states between the Eu(Sr1) and Eu(Sr2) cases. For comparison, the energy have been shifted to be 0 at the position of the highest unoccupied 4f state.

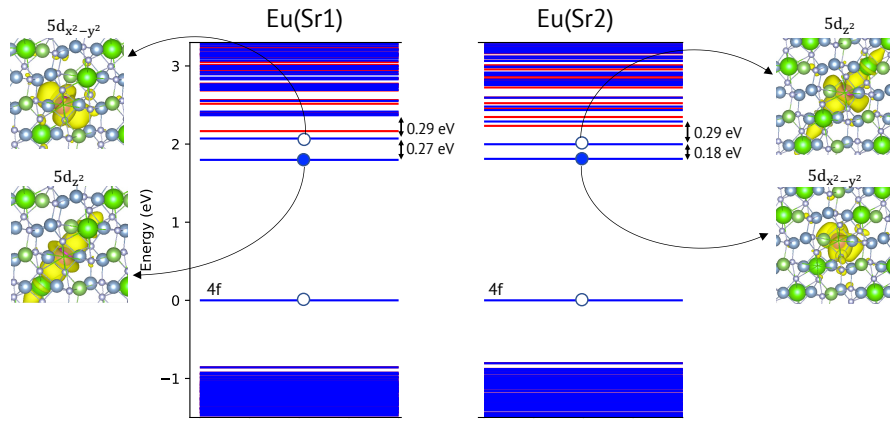


Figure A.7: Kohn-Sham energies computed in the relaxed 288-atoms supercell at the PBE+U level for both Eu(Sr1) and Eu(Sr2) systems, following the constrained occupation method. Blue (red) lines refers to spin up (down) states. For Eu(Sr1), a $5d_{z^2}$ -like orbital is stabilized along the Sr chain while an empty $5d_{x^2-y^2}$ -like state is located in the band gap 0.27 eV above. For Eu(Sr2), a $5d_{x^2-y^2}$ -like orbital is stabilized perpendicular to this Sr chain. The empty $5d_{z^2}$ -like state is located 0.18 eV above. The computed energy separation between the empty 5d states and the conduction bottom (Sr-4d character) is 0.29 eV.

Dominant phonon modes in the Huang-Rhys spectral function

We present in figure A.8 the atomic displacements of the five dominant phonon modes, computed in a $4 \times 4 \times 4$ supercell with 2304 atoms and a total of 6912 possible vibrational modes.

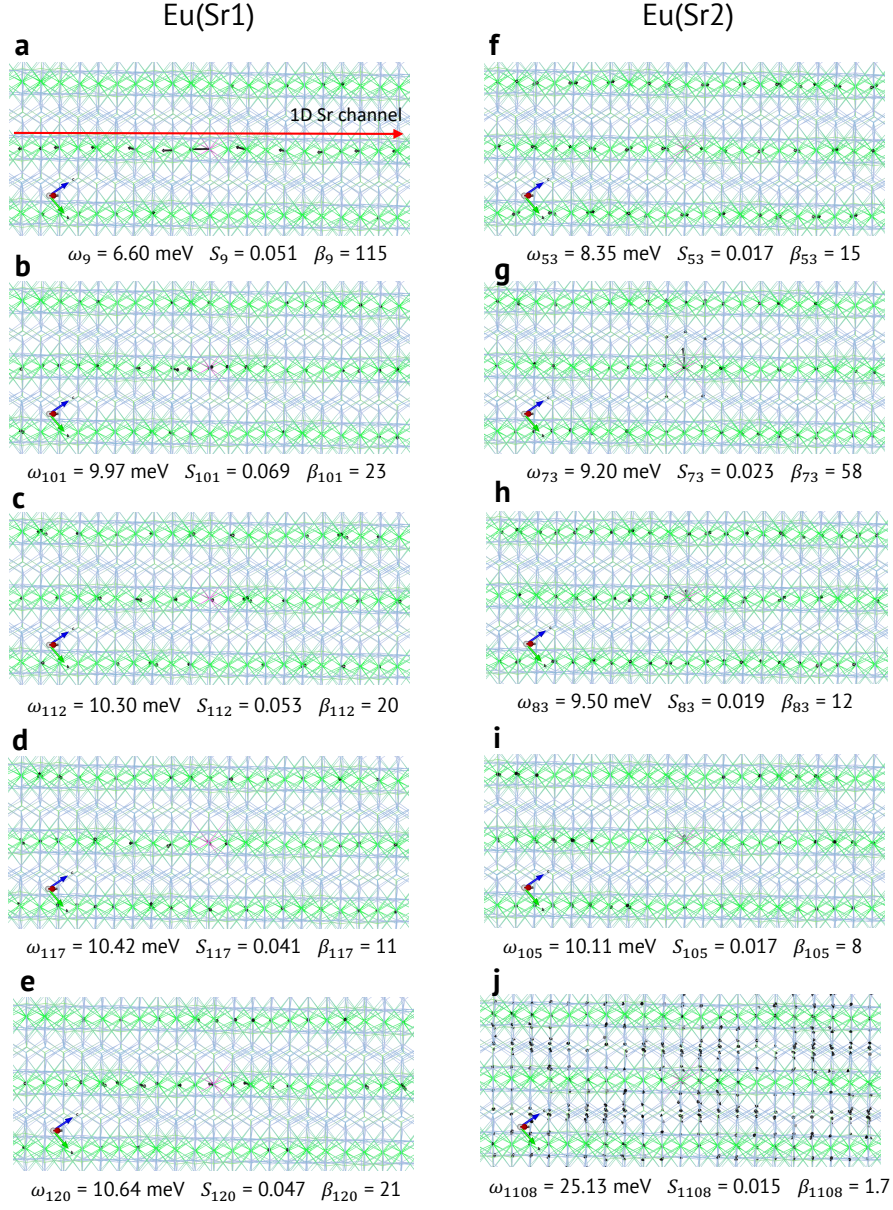


Figure A.8: Atomic displacements associated with the five phonon modes with the highest partial Huang-Rhys factor S_v for **a-e** the Eu(Sr1) and **f-j** the Eu(Sr2) sites, where ω_v is the phonon frequency and β_v indicates the degree of localization. A $\beta_v \approx 1$ describes delocalized modes while a $\beta_v \gg 1$ describes (quasi)-local modes. The displacements arrows have been scaled by 10 for **a-i** and by 20 for **j** for clarity.

Eu(Sr1) PL spectrum with scaled forces

In order to estimate the Huang-Rhys factor S_1 of Eu(Sr1), we have scaled the 5d-4f forces in order to fit the experimental spectrum from reference [161]. We find that scaling the forces by 90% allows to obtain an excellent reproduction of the experimental phonon side-band, as shown figure A.9. It shows that the true S_1 should be around 2.13. This also suggests that the computed forces are slightly overestimated. The origin of this overestimation remains unknown. We note that the Huang-Rhys spectral function is sensitive to the square of the forces ($2.63 \times 0.9^2 \approx 2.13$), highlighting the difficulty in obtaining accurate Huang-Rhys factor and correct ZPL/phonon-side band weights.

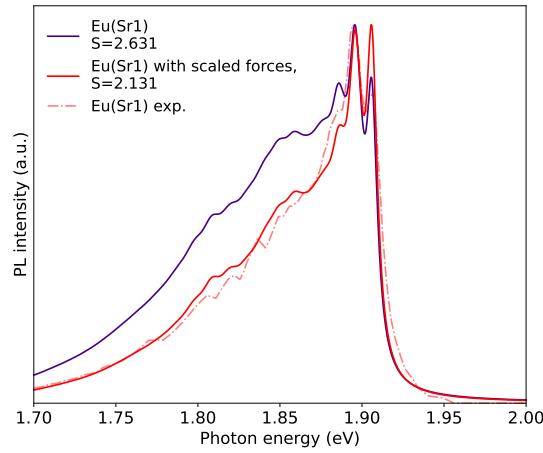


Figure A.9: oK PL spectrum of Eu(Sr1) using 5d-4f forces from first principles, or scaled by 90% or from experiment. The 90% scaling yields an excellent reproduction of the experimental phonon side-band [161]. The reason for the overestimation of the forces remains unknown.

Emission spectrum shift with temperature

We study in this section the temperature evolution of the photoluminescence spectra (PL) emission peak for the two sites and isolate the effect of thermal expansion and ω^3 dependence of the PL intensity $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$.

In figure A.10 we present the temperature evolution of the PL $L(\hbar\omega)$ for the two sites with, and without thermal expansion effect included. In figure A.11 we show the emission peak position as a function of temperature.

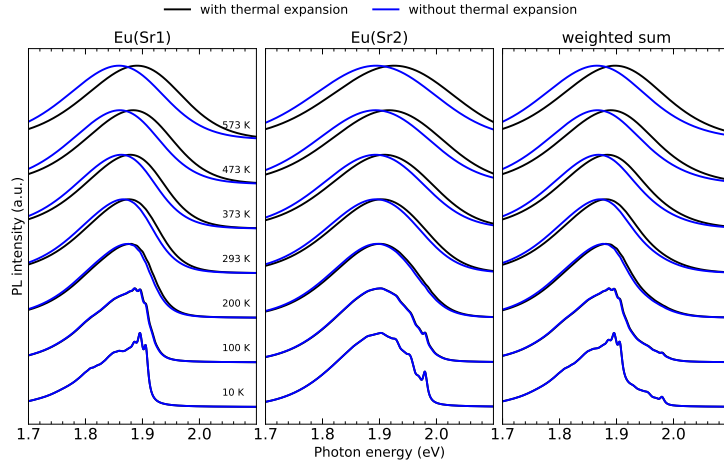


Figure A.10: Photoluminescence intensities of Eu(Sr1), Eu(Sr2) and their weighted sum. Two cases are compared: without thermal expansion and with thermal expansion.

The ω^3 dependence of $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$ causes a blue shift of the emission maximum due to the broadening of the lineshape function $A(\hbar\omega)$ with temperature, even if $A(\hbar\omega)$ does not shift. This fact is illustrated on figure A.12a.

We note that within a semi-classical treatment of the PL spectrum, one can obtain from a one-dimensional configuration coordinate model the emission shift with temperature [77, 203]:

$$E_{em}(T) - E_{em}(0) = \left(\frac{\Omega_g^2 - \Omega_e^2}{\Omega_e^2} + \frac{8\Omega_g^4 \Delta S(0)}{\Omega_e^2 (\Omega_g^2 + \Omega_e^2) E_{em}(0)} \right) k_B T, \quad (\text{A.3})$$

where the Ω_g and Ω_e are the effective frequencies of the ground and excited state. $\Delta S(0)$ is the Stokes shift and $E_{em}(0)$ is the emission

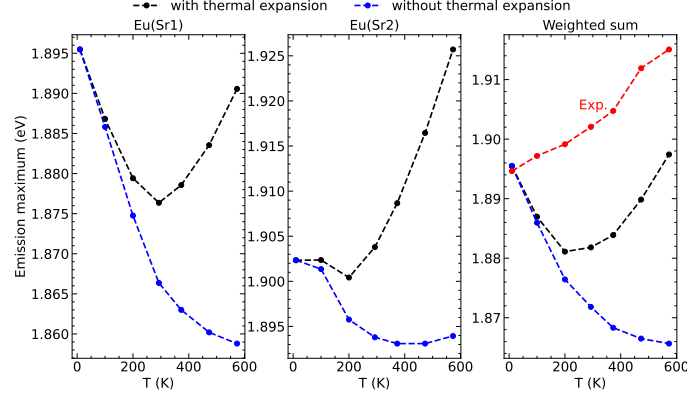


Figure A.11: Photon energy of the emission maximum as a function of temperature for both sites and their weighted sum. Two cases are compared: without thermal expansion and with thermal expansion. In the case of the weighted sum, the experimental data from reference [161] is presented in red.

maximum at 0 K. The first term of equation (A.3) accounts for a potential difference in the Born-Oppenheimer curvatures of the ground and excited state which we find to be negligible for SLA. The second term is obtained when considering the ω^3 dependence. Within this formulation, the vibronic peaks are not treated explicitly and the PL spectrum possesses a gaussian-like shape.

We compare on figure A.12b the shift of equation (A.3) with the difference between the emission maximum of $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$ (blue curve) with the emission maximum of $A(\hbar\omega)$ (green curve). For Eu(Sr1), equation (A.3) yields $E_{em}(T = 573K) - E_{em}(0) = +16$ meV whereas the more accurate computation yields +11 meV. For Eu(Sr2), equation (A.3) yields $E_{em}(T = 573K) - E_{em}(0) = +25$ meV whereas the more accurate computation yields +18 meV. It is worth noting that these discrepancies are reasonable since equation (A.3) is only applicable under conditions of strong electron-phonon coupling.

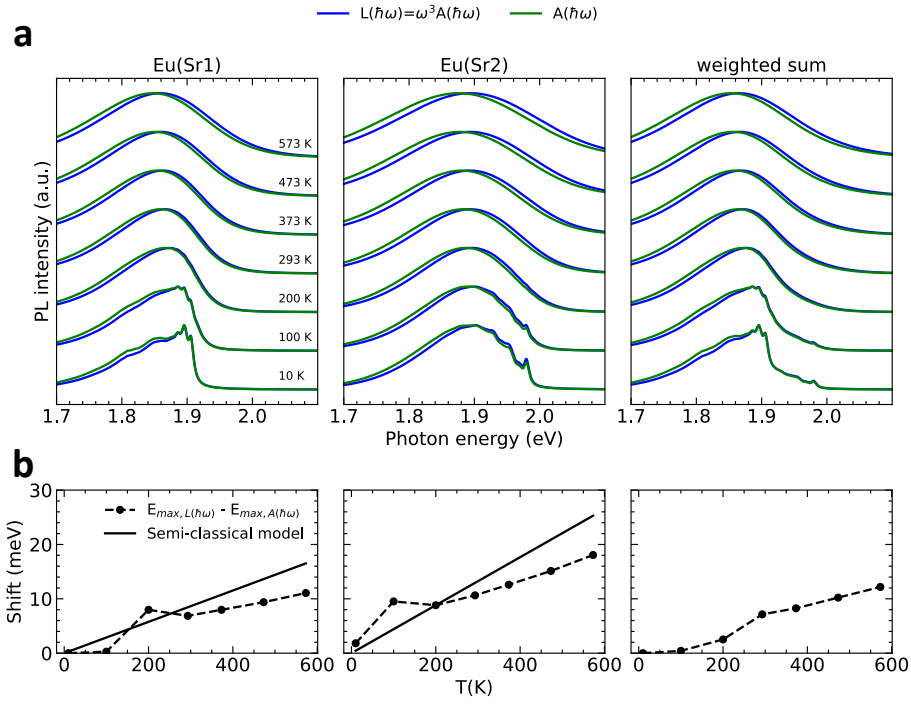


Figure A.12: **a** Temperature dependent PL intensities $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$ (blue curves) of Eu(Sr1), Eu(Sr2) and their weighted sum compared with the lineshape function $A(\hbar\omega)$ (green curves). **b** Shift as computed with equation (A.3) following a semi-classical model (plain lines) compared with the difference between the emission maximum of $L(\hbar\omega) \propto \omega^3 A(\hbar\omega)$ with the emission maximum of $A(\hbar\omega)$ (dotted lines).

B

ENERGY LEVELS AND LUMINESCENCE OF Eu^{2+} AND Eu^{3+} IONS

This appendix aims at providing a qualitative description of the energy levels and associated luminescence properties of the dopant studied in this work, Eu^{2+} . A small comparison with the luminescence from Eu^{3+} ion is also given.

Eu^{2+} has an electronic configuration of $[\text{Xe}]4f^7$. The $4f$ electrons in this state experience minimal interaction with the surrounding crystal field due to the shielding effect of the outer $5s$ and $5p$ orbitals. Eu^{2+} has a $^8S_{7/2}$ ground state and an excited states originating from the $4f^65d^1$ configuration.

The energy separation between these states depends on Coulomb interactions, spin-orbit coupling, and the strength of the crystal field. Optical transitions in Eu^{2+} involve $4f \rightarrow 5d$ transitions, followed by emission from the lowest $5d$ level back to the $4f$ states. These transitions are electric-dipole allowed, leading to broad emission bands due to phonon interactions. The crystal field strongly affects the $5d$ states. This splitting depends on the local coordination geometry and ligand type, significantly impacting the observed emission spectra. The spin-orbit coupling will have an effect on the excited state electron configuration, $4f^65d^1$ (7F_J manifold ($J = 0 - 6$)). For absorption, this means that accounting for spin-orbit interaction is crucial to be predictive [98]. While for emission, the electron will non-radiatively decay to the lowest state of this manifold before photon emission. Focusing on the lowest energy excited state in this multiplet, as done in this work, is hence a reasonable assumption to obtain predictive results.

On the other hand, Eu^{3+} has a $[\text{Xe}]4f^6$ electronic configuration. The $4f^6$ configuration leads to a 7F_J ground-state manifold ($J = 0 - 6$), with excited states arising from intra- $4f$ transitions. These transitions result in well-defined spectral features. Luminescence in Eu^{3+} arises

from ${}^5D_0 \rightarrow {}^7F_J$ transitions, which are parity-forbidden in a free ion but gain intensity through $4f$ - $5d$ and charge-transfer state mixing. The resulting spectra show sharp, well-resolved peaks due to weak coupling with phonons. Spin-orbit coupling contributes significantly to the fine structure of the $4f$ energy levels in Eu^{3+} , resulting in splitting within the 7F_J and 5D_J manifolds [204] on the order of a few hundred of meV and leading to multiple emission lines. The relative intensities of these lines are influenced by the crystal field environment.

HUMAN EYE SENSITIVITY AND CHROMATICITY

The human visual system sensitivity to light is described by the luminous efficiency functions, which quantify how effectively different wavelengths of light stimulate the retina. The eye is most sensitive to wavelengths around 555 nm, corresponding to green light under bright lighting conditions, also known as "photopic" vision. This sensitivity decreases towards the violet and red ends of the spectrum, as shown in figure C.1.

The photopic luminous efficiency function represents how human eyes perceive light of different wavelengths in well-lit conditions. For lower light levels, the "scotopic" luminous efficiency function dominates, reflecting the increased sensitivity of rod cells to shorter wavelengths in dim environments [205, 206].

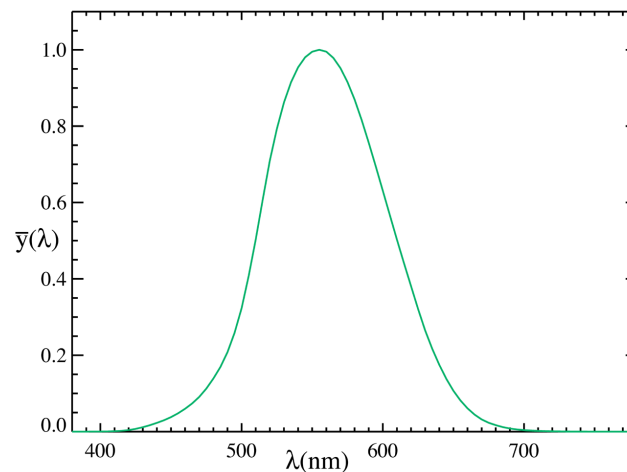


Figure C.1: Photopic luminous efficiency function.

Color perception is based on the differential response of three types of cone cells in the retina, each sensitive to different ranges of wavelengths:

short (S-cones, peaking at 420 nm), medium (M-cones, peaking at 530 nm), and long (L-cones, peaking at 560 nm) wavelengths. The brain interprets the combined responses of these cone cells to perceive color [207].

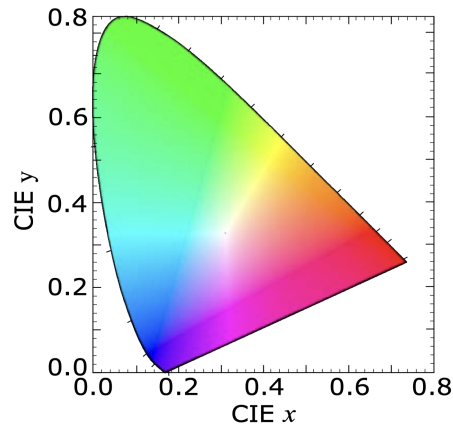


Figure C.2: CIE 1931 Chromaticity Diagram, showing the range of visible colors.

The CIE 1931 chromaticity diagram [208] (figure C.2) represents color as a function of the chromaticity coordinates. These coordinates are derived from the human visual system's response to the entire visible spectrum. They describe chromatic properties and perceived brightness, making the chromaticity diagram widely used in lighting and display design.

Maximizing luminous efficacy requires tailoring light sources to the eye's sensitivity, especially around the green part of the spectrum. Chromaticity coordinates are also crucial for determining the color temperature of light sources, ensuring suitability for different applications.

USE OF LARGE LANGUAGE MODELS

The author would like to acknowledge the use of Large language Model and natural language processing tools for assisting with English corrections, grammar improvements, and light rephrasing of unclear sentences. While these tools were used during the editing process, the final content and interpretations presented in this manuscript are solely the author own work.

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