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Quantitative assessing of crystal field, nephelauxetic, and Stokes shift effects on the blue luminescence of Eu$^{2+}$ ions incorporated in ZnS films

Victor Hugo López-Lugo, Martha Judith Rivera-Medina and Juan Carlos Alonso-Huitrón

Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico. Apartado Postal 70-360, Coyoacan 04510, Ciudad de Mexico, Mexico

E-mail: alonso@unam.mx

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Abstract

A quantitative study of the crystal field, nephelauxetic, and Stokes shift effects on the 5d $\rightarrow$ 4f levels of Eu$^{2+}$ ions incorporated in ZnS films is presented. The magnitude of the crystal effect was calculated using the simplest point charge model to express the crystal field splitting of Eu$^{2+}$ 5d orbitals surrounded by four $S^2^-$ ligands in tetrahedral coordination symmetry. The shift of the centroid of the 5d levels by nephelauxetic effect was analyzed using a model that involves the polarizability of the anion ligands, similar to that used to investigate this effect for Ce$^{3+}$ in many inorganic compounds. The Stokes shift was evaluated according to the Frank-Condon principle, under the idealized situation where the Stokes shift and the emission bandwidth can be expressed in terms of the Huang-Rhys parameter. We found that the redshift ($\Delta E_{5d} = 0.32$ eV) of the 5d $\rightarrow$ 4f transition for the free Eu$^{2+}$ ion, due to crystal field splitting was half of the redshift due to the nephelauxetic effect. This result is consistent with the large size, large polarizability, and low electronegativity of the sulfide ions. We also found a relatively large Stokes shift which can be attributed to the autoionization of the 5d electrons to the conduction band levels. The total redshift of the 5d and 4f energy levels with respect to the 5d and 4f energy gap for a free Eu$^{2+}$ in vacuum fits quite well with the blue luminescence peaked at 2.73 eV for Eu$^{2+}$ ions incorporated in the ZnS films. Based on the experimental results and the calculations for the crystal field splitting, nephelauxetic, and Stokes shift effects, we also propose a simplified energy band and levels diagram which helps to explain the excitation-emission mechanisms of the blue luminescence of the Eu$^{2+}$ ions incorporated in the ZnS films.

1. Introduction

Rare earth substituted inorganic phosphors have gained significant attention in the last decade; and nowadays, they are considered as one of the most promising luminescent materials. In fact, they have been extensively used for efficient white light-emitting devices and other multi-color electroluminescent devices [1–6]. Among the lanthanide activator ions, the Eu$^{2+}$ and Ce$^{3+}$ ions have been the most intensively investigated because they show very efficient broadband luminescence due to parity allowed electric dipole transitions between 4f$^{n}5d^{l}$ excited states and 4f$^{n}$ ground states (n = 1 for Ce$^{3+}$ and n = 7 for Eu$^{2+}$). The extensive use of these ions is also because of the large energy difference (energy gap) between the 4f$^{n-1}5d^{1}$ and 4f$^{n}$ energy levels (hereafter denoted as 5d and 4f levels, respectively) for the free Eu$^{2+}$ (4.2 eV; 33871 cm$^{-1}$) and Ce$^{3+}$ (6.35 eV; 51210 cm$^{-1}$) can be substantially decreased to the visible spectrum when these ions are incorporated in different crystalline host inorganic compounds. The spectral tuning of the luminescence is because the excited 5d orbitals are strongly affected by the surrounding anion ligands, meanwhile, the well-shielded 4f levels are less affected. Several well-detailed reviews publications have identified that when Eu$^{2+}$ (or Ce$^{3+}$) ions are accommodated substituting a metal cation in a crystalline host, the energy gap between the 5d and 4f levels of the free ions, $E_{\text{free}}$, is lowered by...
an amount, D(A), which is referred to as the redshift, where A is the host crystal \([3, 7, 8]\). This redshift is dictated by two major effects: the nephelauxetic effect and crystal field splitting, which are discussed more in detail further in the text. Besides this redshift, there is a Stokes shift, denoted as \(\Delta S(A)\), in the emission energies coming from the optical transitions between the coupled vibrational-electronic 5d and 4f levels, as prescribed by the Frank-Condon principle.

The energy of the first 5d \(\rightarrow\) 4f transitions of Eu\(^{2+}\) incorporated in more than 300 different crystalline inorganic compounds (fluorides, chlorides, bromide, iodides, oxides, sulfides, selenides, nitrides, aluminates, silicates, etc) has been compiled and resulting following trends:[7]. The emission energy is around (3.1 eV; 25000 cm\(^{-1}\)) for the fluorides and shifts toward (2.75 eV; 22177 cm\(^{-1}\)) moving down in the halogen group. In the oxides the emission varies from the ultraviolet at (3.44 eV; 2774 cm\(^{-1}\)) to beyond (2.07 eV; 16693 cm\(^{-1}\)). Emission in the sulfides and the selenides is generally at longer wavelengths than in the oxides. These trends have been explained based on the phenomenological predictive equation

\[
E_{\text{em}}(A) = E_{\text{free}} - D(A) - \Delta S(A) \tag{1}
\]

The redshift due to crystal field splitting and the centroid shift due to nephelauxetic effect has been extensively and quantitatively studied for the Ce\(^{3+}\) 5d levels \([9-14]\). These studies have shown that the magnitude of the crystal field splitting depends on the coordination number, the symmetry of the activator-ion sites, the size of the substituted cations, and the degree of polyhedral distortion around the Ce\(^{3+}\) ion. Whereas, the centroid shift by nephelauxetic effect depends on the polarizability of the surrounding anion ligands and on the covalency (sharing of electrons) of the chemical bonds between the metal activator cation and the anion ligands.

Intriguing that the exhaustive compilation of the energy of the 5d \(\rightarrow\) 4f transitions of Eu\(^{2+}\) does not include ZnS as a host crystal, even though it unveils data for binary sulfide host, such as BaS, MgS, SrS, and MgS. However, the data for Eu\(^{2+}\) incorporated in ZnS were not included in this compilation \([7]\). Moreover, ZnS has been widely used as excellent phosphor material to host a variety of metal transition and rare earth luminescent centers. Especially, Eu\(^{2+}\) ions incorporated in ZnS in the form of nanocrystals, nanoparticles, and thin films is becoming an important phosphor due to its blue emission peaked in the range from (2.58 eV; 20806 cm\(^{-1}\)) to (2.95 eV; 23790 cm\(^{-1}\)) \([15-22]\). ZnS has been also attracted renewed interest in its mechanoluminescence (ML) and electroluminescence (EL) applications \([23, 24]\). In this work, we report a quantitative study of the nephelauxetic, crystal field, and Stokes shift effects for Eu\(^{2+}\) incorporated in ZnS, in order to explain the blue luminescence of this phosphor.

2. Experimental details

2.1. Preparation of films

The ZnS:Eu\(^{2+}\) thin films whose luminescent properties were investigated and modeled in this work were deposited on glass substrates by ultrasonic spray pyrolysis, using zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}]\) (0.724 g, 3.30 mmol), 1,3-dimethyl-2-thiourea \([\text{CH}_3\text{NHCSNHCH}_3]\) (0.521 g, 5.00 mmol) and europium chloride hexahydrate \([\text{EuCl}_3 \cdot 6\text{H}_2\text{O}]\) (0.037 g, 0.10 mmol, 3 molar% of zinc). These solids were mixed and subsequently added to a solution of anhydrous methanol (71.2 ml), deionized water (23.8 ml), and acetic acid (5 ml). The substrate temperature was 450 \(^\circ\text{C}\), and air was used as the carrier and director gas with constant flow rates fixed at 1.5 l min\(^{-1}\) and 0.3 l min\(^{-1}\), respectively. Under these deposition conditions, 550 nm thick ZnS:Eu\(^{2+}\) films were obtained using 10 ml of the precursor’s solution, during 15 min of deposition. The deposition rate of the films was 36.7 nm/min. All reagents were purchased from Sigma Aldrich and used as received without further purification. The air used for the spray pyrolysis deposition process was provided from an oil-free air compressor. Undoped ZnS films were deposited under the same conditions but using a solution without europium chloride.

2.2. Microstructure of films

Figure 1 shows the XRD pattern for the ZnS: Eu\(^{2+}\) film and that for an undoped ZnS film deposited under the same spray pyrolysis conditions. Using the card number 00005-0492 from the PDF-2(2004) database, both patterns were identified as corresponding to the hexagonal wurtzite ZnS crystalline structure. Both films are polycrystalline with the preferential orientation of the crystals in the (002) and (103) planes. All the other XRD peaks also correspond to the hexagonal phase of ZnS, although the ZnS:Eu\(^{2+}\) film presents more diffraction peaks than the ZnS film. The average crystallite size, calculated from the Debye-Scherrer formula was: \(D = 24.0\ \text{nm}\) and \(D = 24.8\ \text{nm}\) for the ZnS:Eu\(^{2+}\) and ZnS films, respectively, and the corresponding lattice parameters of the crystals are indicated inside figure 1. The additional diffraction peaks that appeared for Eu-doped ZnS films compared to pure ZnS films correspond to other crystal orientations of the ZnS phase. The absence of diffraction peaks corresponding to any phase of Eu based compound indicates that the level of Eu doping is very low. This is consistent with the failed attempt to detect the amount of Eu atoms incorporated in
the ZnS:Eu films by energy dispersive spectroscopy and x-ray photoelectron spectroscopy, whose minimum limit of detection is ~1%.

These results on the structure of the ZnS:Eu$^{2+}$ are consistent with those reported in other research works on this topic, which indicates that the Eu$^{2+}$ ions enter in the ZnS hexagonal wurtzite lattice, substituting the Zn$^{2+}$ ions [16, 20, 22, 25, 26]. The small variations in the lattice parameters indicate some degree of polyhedron distortion around the Eu$^{2+}$ ion, due to the larger ionic radius of Eu$^{2+}$ (1.09–1.12 Å), compared to that of Zn$^{2+}$ (0.74 Å) [22, 25, 27]. We addressed the calculation of the crystal field splitting and centroid shift based on the microstructural results under the assumption that the Eu$^{2+}$ 5$d$ orbitals are surrounded by four-point charges in tetrahedral coordination symmetry.

2.3. Luminescent properties of films

Figure 2 shows the typical excitation and emission spectra of the films, as a function of wavelength. In this case, the emission spectrum was recorded by fixing the excitation wavelength at 332 nm, while the detection wavelength of the spectrophotometer was scanned from 350 to 650 nm. The excitation spectrum was recorded by fixing the emission wavelength at 454 nm, where the maximum emission occurs, while the excitation wavelength was varied from 200 to 400 nm.

Figure 3 shows the normalized excitation and absorption spectra as a function of photon energy. As can be seen the energy for the maximum of excitation coincides with the energy for the maximum of the optical absorption (3.75 eV).

At this point, it is important to highlight that the blue luminescence of the films is a strong indication of the incorporation of Eu$^{2+}$ in the ZnS matrix. It is known that Eu$^{3+}$ is commonly incorporated in many luminescent hosts doped with Eu, resulting in red luminescence. In the case where the films are made in the air, the conversion of Eu$^{3+}$ to Eu$^{2+}$ should be completed via annealing in reducing gas like forming gas H$_2$/N$_2$ mixture. In this work, ZnS doped by Eu$^{2+}$ can be simply obtained in air, resulting in blue luminescence. One explanation
of this result is that the thermal process involving H$_2$S generated from thiourea acts as a reducing agent giving rise to direct thermal reduction of Eu$^{3+}$ to Eu$^{2+}$ during the synthesis of ZnS under aerobic conditions [22, 28]. The result is quite similar to blue luminescence of Eu$^{2+}$ doped borates prepared by spray pyrolysis in air reported by Cocivera’s group in Canada, where they attributed the unusual phenomena to the specific group of borates [29, 30].

3. Theory

In order to investigate the emission of Eu$^{2+}$ incorporated in ZnS and the relation between redshift and Stokes shift and the crystalline environment, we used equation (1) and a method similar to the method followed to investigate Ce$^{3+}$ 5d—4f transitions in crystalline compounds [9–14]. Although both, the nephelauxetic and crystal field splitting effects operate and contribute simultaneously to the redshift by convenience they have been studied and theoretically model individually in the ligand-field theory [31]. Thus, in order to calculate the contribution of each effect to the redshift, $D(A)$, it can be expressed as

$$D(A) = \epsilon_{n}(A) + \epsilon_{cf}(A)$$

where $\epsilon_{n}(A)$ is the centroid shift due to the nephelauxetic effect and $\epsilon_{cf}(A)$ is the difference in energy between the centroid and the lowest 5d levels, originated by the crystal field splitting.
3.1. Crystal field splitting and nephelauxetic effect

The magnitude of \( \epsilon_{cf}(A) \) was calculated based on the expression for the crystal field splitting for Eu\(^{2+}\) 5d orbitals (separation between the highest and lowest 5d energy levels) surrounded by four ligands in tetrahedral coordination symmetry (T\(_d\)). According to the simplest point charge model, the magnitude of \( \epsilon_{cf}(A) \) can be expressed as [27, 31, 32]:

\[
\epsilon_{cf}(A) = \frac{4}{9}(+6)D_q
\]

where the term, \( D_q \), is the radial parameter determined by the formula:

\[
D_q = \frac{1}{6}z'\epsilon^2\frac{(r^4)}{R^5}
\]

where \( z' \) is the effective anion ligand charge, \( \epsilon \) is the electron charge, \( r \) is the radius of the 5d wave function, and \( R \) is the cation-anion bond length.

The centroid shift \( \epsilon_{cn} \) by the nephelauxetic effect of the 5d levels with respect to the 4f levels for Eu\(^{2+}\) can be calculated using the formula developed in previous quantitative studies of this effect in Ce\(^{3+}\) incorporated in different ionic crystals, which is [9, 14, 33]:

\[
\epsilon_{cn}(A) = \frac{e^2}{4\pi\epsilon_0}[(r^2_{5d}) - \langle r^2_{4f} \rangle] \sum_{i=1}^{N} \frac{\alpha_i}{(R_i - f\Delta R)^6}
\]

where, in our case, \( r \) represents the position of the electron in either the 5d or 4f orbital of Eu\(^{2+}\), and \( \langle r^2 \rangle \) is the expectation value of \( r^2 \). \( \alpha_i \) is the polarizability of anion \( i \) located at a distance \( R_i \) from the Eu\(^{2+}\) ion in the unrelaxed lattice. The summation is over all \( N \) coordinating anion ligands. \( f\Delta R \) is a correction term to incorporate lattice relaxation around the cation assuming, in a crude approximation, that each anion relaxes radially by a fraction \( f \) of the difference \( \Delta R \) in ionic radius between Eu\(^{2+}\) and the cation for which it substitutes.

3.2. Stokes shift

The Stokes shift comes from the interaction of the dopant ion with the vibrations of the lattice. The simplest model to account for the interaction between the dopant ion and the vibrating lattice is the single configurational coordinate model. In this model, we consider only one vibrational mode, i.e. the so-called breathing mode in which the surrounding lattice pulsates in and out around the dopant ion. This mode is assumed to be described by the harmonic model. As a first approximation, it can be assumed that the lattice phonon energies \( \hbar\omega \) are the same for the 4f ground state as for the 5d excited states, and consequently, the plots of the energy for these states in the configurational coordinate diagram are parabolas with the same curvature.

Under this idealized situation and according to the Frank-Condon principle, the Stokes shift can be expressed in terms of the Huang-Rhys parameter \( S \) as [7, 34]:

\[
\Delta S(A) = (2S - 1)\hbar\Omega
\]

and \( S \) is related with the full width at half maximum (FWHM), \( \Gamma(T) \), of the luminescent emission band through the formula:

\[
\Gamma(T) = 2.36\hbar\Omega\sqrt{S} \sqrt{\coth\left(\frac{\hbar\Omega}{2k_B T}\right)}
\]

where \( T \) is the absolute temperature, \( k_B \) is the Boltzmann constant and \( \hbar\Omega \) is the phonon energy of the vibrating bonds.

4. Results and discussion

As figure 1 shows the energy of the emission of the Eu\(^{2+}\) ions incorporated in the ZnS:Eu\(^{2+}\) films is centered at \( E_{em}(ZnS) = 2.73 \) eV (454 nm). Therefore, the experimental shift of this emission with respect to the emission as a free ion is: \( \Delta E = 1.47 \) eV = \( \epsilon_{cn} + \epsilon_{cf} + \Delta S \). Based on this we proceeded first to calculate the Stokes shift, then the crystal field shift and finally the shift by the nephelauxetic effect.

4.1. Calculation of the Stokes shift

The Stokes shift was calculated using the formulas (6) and (7). Figure 4 shows the normalized luminescent emission spectra as a function of wavenumber, obtained at room temperature \( (k_B T = 201.6 \) cm\(^{-1}\)), for different excitation wavelengths. A small dependence on the FWHMs of the PL spectra was observed upon different excitation wavelengths. Therefore, \( \Gamma(T) = 4065 \) cm\(^{-1}\) ± 5% was chosen as the average of these FWHMs. As the value of the phonon energy, we used the average \( (\hbar\Omega = 1142 \) cm\(^{-1}\)) of the wavelengths assigned to the
symmetric (1164 cm\(^{-1}\)) and asymmetric (1120 cm\(^{-1}\)) stretching vibrations of Zn-S bonds in ZnS films and nanoparticles with hexagonal structure [35–37]. The calculated value of the Stokes shift is \(\Delta S = 4032\) cm\(^{-1}\). This value is slightly larger than 4000 cm\(^{-1}\) indicating that the emission begins to be ‘anomalous’, and there can be auto-ionization of the 5d electron to conduction band levels [7].

4.2. Calculations of the radial parameters, bond lengths, and crystal field shift

The radial parameters \(\langle r^p \rangle\), \(p = 1, 2 \) or \(4\) were calculated using the expressions:

\[
\langle r^p \rangle_{n,l} = \int_0^\infty [rR_{n,l}] r^p [rR_{n,l}] dr
\]

where \(R_{n,l}\) are the hydrogenic radial wavefunctions [38]:

\[
R_{n,l}(\rho) = \frac{2Z^*}{n^*a_0} \frac{1}{\rho} \frac{2l+1}{l!} \frac{(n^*-l-1)!}{2n^*[(n^*+l)!]} e^{-\rho} \tau_{l,p}^{n,l+1}(\rho)
\]

where \(\rho = \frac{2Z^*}{n^*a_0}\), and \(L_{2l+1}(r)\) are the Laguerre polynomials, \(Z^*\) is the nuclear effective charge, and \(n^*\) is the effective quantum number defined by Slater [39]. Since the calculation of the Laguerre polynomials requires integer numbers, in this work we used, \(n^*=4\) instead of \(n^*=3.7\) for \(n = 4\), and \(n^*=4\) for \(n = 5\). The bond length between zinc and sulfur ions, \(d_{ZnS}\), was calculated using the value of the lattice parameters for ZnS:Eu\(^{2+}\) [22], for the wurtzite structure, \(a = 3.862\) Å and \(c = 6.225\) Å, using the formulas \(d_{ZnS} = c \cdot u\),

\[u = \frac{1}{4} + \left(\frac{5}{8}\right) \left(\frac{a}{c}\right)^2\]

The value obtained was \(d_{ZnS} = 2.35\) Å. The bond length or the distance between the S\(^2-\) anion and the Eu\(^{2+}\) cation was calculated, as the sum of the radius of these ions, \(R = r_{S}^{2-} + r_{Eu}^{2+}\). The radius of the S\(^2-\) anion, was calculated from \(d_{ZnS} = 2.35\) Å, using the Linus Pauling model [41], and the obtained value was \(r_{S}^{2-} = 1.76\) Å. This value is close to the average of the crystal radius and the effective ionic radius reported for this ion in chalcogenides [42]. Whereas for the Eu\(^{2+}\) ion radius, \(r_{Eu}^{2+}\), we used the radius calculated for the 5 s orbital of this ion, \(r_{5s}^{2+} = r_{5s} = 1.12\) Å. This value is reliable considering that it close to the average of those reported for the crystal radius and effective ionic radius of Eu\(^{2+}\) [25, 27, 43]. The values of the radial parameters for the Eu\(^{2+}\) orbitals, calculated using Wolfram Mathematica 11.3, as well as the Eu-S bonds length \(R\), and \(\Delta R = R - d_{ZnS}\) are given in table 1.

The shift due to crystal field splitting, \(\epsilon_{cb}\), was calculated using equations (3) and (4) implementing the calculated radial parameters for the Eu\(^{2+}\) orbitals. We used \(z' = 2 \cdot (0.79)\) as the value of the effective sulfur anion ligand charge, where 0.79 is the fractional ionic character of bonds in similar metal-chalcogenide crystals [44]. The obtained value for \(\epsilon_{cb}\) is shown in table 2. It is a relatively small redshift due to crystal field splitting of the Eu\(^{2+}\) 5d levels within the ZnS compared to other compounds based on halides and oxides mainly due to the larger size of the sulfur ion [7].

4.3. Centroid shift by nephelauxetic effect

As mentioned in section 3.1, the centroid shift \(\epsilon_{cn}\) by nephelauxetic effect can be calculated from equation (5), which requires the knowledge of the coordination number and the polarizability of the N coordinating anion ligands at distance \(R\), from the Eu\(^{2+}\) ions. In our case, given the experimental results and discussion on the
microstructure of the ZnS: Eu$^{2+}$ films, we can assume that each Eu$^{2+}$ is tetrahedrally surrounded by four S$^{2-}$ ligands, and therefore $N = 4$, $R = R_w$ where $R$ is the distance between the Eu$^{2+}$ cation and the S$^{2-}$ anion ligands and $\alpha_i = \alpha$ is the polarizability of the S$^{2-}$ anions. It has been recently remarked in some recent works, that a quantitatively assessing of the anions polarizability remains challenging. Therefore, it is not a straightforward calculation for the centroid shift values by using equation (5) [9]. In fact, equation (5) has been rather used to calculate the polarizability of anions ligands surrounding Ce$^{3+}$ at distances $R_i$ in different inorganic compounds, using the experimentally observed centroid shift $\epsilon_c$, and a value for the relaxation parameter of $f = 0.5$ [10, 11, 13, 14]. Actually, for other compounds, the relaxation correction has been neglected ($f = 0$) [12]. Even though, there is no strict criterion to choose a fraction value of $f$, due to the lack of detailed information on the lattice relaxation processes, it has been established that large values of $f$ may be expected. For example in Ce$^{3+}$ cation systems, a large value of $f$ was observed whenever Ce$^{3+}$ substitutes to a divalent site mainly attributed to the excess of positive charge [14]. Whereas for our case we may expect a relaxation parameter within values in the range: 0 $\leq f < 0.5$. Based on the experimental data for the emission shift, $\Delta E = 1.47$ eV, and the calculated values for $\Delta S = 0.5$ eV and $\epsilon_c$ = 0.32 eV, the expected value of the centroid shift is: $\epsilon_c$ = 0.65 eV. This shift along with the other shift values and the relevant energies are listed in table 2.

The polarizability of the S$^{2-}$ for different values of $f$ was calculated by the substitution of the centroid shift in formula (5), resulting in $f = 0.002$ and polarizability of $\alpha = 3.4A^3$. The latter is acceptable for sulfur-based compounds derived from hydrocarbon molecules [45]. For $f = 0.016$ a value, $\alpha = 3.15A^3$ was obtained which does not differ as much of the polarizability of the S$^{2-}$ ion calculated using the quantum-theoretical expression derived for ions with closed-shell electronic configuration [46, 47]. The fact that we obtained acceptable values of the polarizability of S$^{2-}$ ions, only for very low values of $f$ indicates that the effect of lattice relaxation around the Eu$^{2+}$ cation is small, and this is consistent with the fact that the lattice parameters of the ZnS: Eu$^{2+}$ and the ZnS films do not differ very much [22]. The fact that the redshift of the 5d level due to nephelauxetic effect is the double of the redshift due to crystal field splitting is consistent with the fact that the S$^{2-}$ anion is one with the lowest electronegativity or higher tendency to lose electrons in the nephelauxetic series [12, 31].

### 4.4. Model of excitation-emission mechanisms

As table 2 shows, the calculated total redshift, $D + \Delta S = 1.47$ eV, of the 5d and 4f energy levels with respect to the 5d and 4f energy gap ($E_{free} = 4.2$ eV) for a free Eu$^{2+}$ in a vacuum, fits quite well with the blue luminescence peaked at 2.73 eV the Eu$^{2+}$ ions incorporated in the ZnS films. Based on the experimental results and our calculations, we built the simplified energy band and energy levels diagram depicted in figure 5, which helps to

| Table 1. Radial parameters calculated for the different Eu$^{2+}$ orbitals, and the Eu-S bonds length, $R$, and $\Delta R$. |
|-----------------|-----------------|-----------------|
| Orbital         | Radial parameter | Value           |
| Eu$^{2+}$ (5d)  | $(r)_h$         | 1.37 Å          |
| Eu$^{2+}$ (5s)  | $(r)_l$         | 1.12 Å          |
| Eu$^{2+}$ (5p)  | $(r)_v$         | 1.0 Å           |
| Eu$^{2+}$ (5d)  | $(r)_v$         | 1.47 Å          |
| Eu$^{2+}$ (5d)  | $(r)_v$         | 1.47 Å          |
| R               |                 | 0.52 Å          |
| $\Delta R$     |                 | 0.52 Å          |

| Table 2. Parameters associated with the emission energy due to transitions between 5d $\rightarrow$ 4f levels of Eu$^{2+}$ ions incorporated in ZnS films. |
|-----------------|-----------------|-----------------|
| $E_{free}$      | 4.2 eV          | 33871 cm$^{-1}$ |
| $E_{em}(ZnS)$   | 2.73 eV         | 22016 cm$^{-1}$ |
| $\Delta E$      | 1.47 eV         | 11855 cm$^{-1}$ |
| $\Delta S$      | 0.5 eV          | 4032 cm$^{-1}$  |
| $\epsilon_c$    | 0.32 eV         | 2582 cm$^{-1}$  |
| $\epsilon_m$    | 0.65 eV         | 5645 cm$^{-1}$  |
| $D$             | 0.97 eV         | 8064 cm$^{-1}$  |
| $D + \Delta S$  | 1.47 eV         | 12097 cm$^{-1}$ |
model the excitation-emission mechanisms of the luminescence of the Eu$^{2+}$ ions incorporated in the ZnS films. As figure 2 shows, the optical absorption has its peak or maximum at 3.75 eV, which corresponds to the bandgap of the ZnS matrix. The fact that the excitation spectrum shown in figure 2 has its maximum at the same energy suggests that the 5d-4f transitions are activated more efficiently when the electrons are excited from the edge of the valence band to the edge of the conduction band. The excitation spectrum also shows an onset where it starts to rise significantly, at 3.56 eV, which suggests that photons with this energy excite electrons from the valence band of the ZnS matrix to the 5d electronic levels of the Eu$^{2+}$ ions. It is worth mentioning that, a photon has a lower probability to excite electrons from the valence band to the Eu$^{2+}$ 5d levels than to excite electrons from the valence band to the conduction band, because the density of 5d levels is much smaller than the density of levels in the conduction band, and this explains the smaller intensity of the excitation spectrum at the onset energy. The closeness of the electronic 5d level to the conduction band is consistent with the high value found for the Stokes shift, which suggests that there can be auto-ionization of the 5d electrons to conduction band levels.

5. Conclusions

In order to explain the blue luminescence of Eu$^{2+}$ ions incorporated in ZnS films, the redshifts of the 5d levels of Eu$^{2+}$ due to the crystal field ($\epsilon_{cf}$) and nephelauxetic ($\epsilon_{na}$) effects have been calculated by applying the simplest point charge model and the ligand polarization model, respectively. The stokes shift ($\Delta S$), was also calculated using the idealized situation where at first approximation $\Delta S$ and the emission bandwidth are expressed in terms of the Huang-Rhys parameter and the lattice phonon energy. We found that the redshift due to crystal field splitting, $\epsilon_{cf} = 2419 \text{ cm}^{-1}$(0.32 eV) was relatively smaller than the redshift by nephelauxetic effect, $\epsilon_{na} = 5645 \text{ cm}^{-1}$(0.65 eV), which was expected given the large size and the large polarizability of the sulfide ions. The relatively high value obtained for the Stokes shift, $\Delta S = 4032 \text{ cm}^{-1}$ (0.5 eV) indicates that it can be some ‘anomalous’ emission that involves autoionization of electrons from 5d to conduction band levels. From the calculated and experimental parameters, a simplified energy band and energy levels diagram was proposed which helps to explain the excitation-emission mechanisms of the blue luminescence of the Eu$^{2+}$ ions incorporated in the ZnS films.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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