

A ligand field theory-based methodology for the characterization of the $\text{Eu}^{2+} [\text{Xe}]4f^65d^1$ excited states in solid state compounds

Amador García-Fuente^a, Fanica Cimpoesu^b, Harry Ramanantoanina^a, Benjamin Herden^a, Claude Daul^a, Markus Suta^c, Claudia Wickleder^c, Werner Urland^{a,*}

^a Department of Chemistry of the University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland

^b Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 060021, Romania

^c Inorganic Chemistry, Faculty of Science and Engineering, University of Siegen, Adolf-Reichwein-Straße, 57068 Siegen, Germany

The theoretical rationalization of the open-shell 4f and 5d configuration of Eu^{2+} is by far not trivial because it involves a non-standard version of ligand field theory, based on a two-shell Hamiltonian. Here we present our methodology based on ligand field theory, taking the system $\text{CsCaBr}_3:\text{Eu}^{2+}$ as a case study with an octahedral coordination sphere of Eu^{2+} . The ligand field, interelectronic and spin-orbit coupling parameters are deduced from experimental data. The assignment of the transitions to the corresponding irreducible representations of the double group was performed together with the intensity modelling resulting in an excellent match to the experimental spectra.

1. Introduction

The search for new materials with interesting luminescence properties and a low energetic demand has become one of the most interesting topics in modern science, especially since the ban of old fashioned incandescent light bulbs in the European Union, which consume more than 90% of the incoming energy as heat. Nowadays, artificial white light can be obtained for instance by the combination of a GaN blue LED with an inorganic phosphor, such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Yttrium Aluminium Garnet, YAG) doped with Ce^{3+} [1]. This system has already been extensively used as a white light source in many common objects, such as traffic lights, car headlights or marking lamps in tunnels. However, the combination of the blue light of the LED with the yellowish spectrum of Ce^{3+} results in a light source, which is bluish cold and thus being far from the perception of natural (warm) sunlight. In order to obtain a better approach to warm-white light, one option is to add a second phosphor with a strong red component to the system or to combine a UV LED with at least three (red, green and blue) phosphors. In this sense, phosphors created by doping of a host lattice with trivalent lanthanide ions have been extensively studied experimentally during the last decades and have also been already used in applications. A well-known example is Eu^{3+} activated Y_2O_3 showing red luminescence at 610 nm [2] that is used in low-pressure mercury

discharge lamps [3]. The theoretical prediction of their line spectra due to intraconfigurational $[\text{Xe}]4f^n \rightarrow [\text{Xe}]4f^n$ transitions by computational methods has also advanced during the last 50 years, based on the foundations of Judd and Ofelt [4,5], which have also been refined by relativistic methods [6,7].

Due to the electric-dipole forbidden character of the $[\text{Xe}]4f^n \rightarrow [\text{Xe}]4f^n$ transitions and the respective low quantum efficiencies, divalent lanthanides are a more promising alternative. The electric-dipole allowed $[\text{Xe}]4f^n \rightarrow [\text{Xe}]4f^{n-1}5d^1$ transitions lead to much higher intensities and are thus interesting from an applicational perspective [8]. Moreover, since the 5d orbitals are much less well-shielded than the 4f orbitals, their energetic positions are more prone to changes in the crystal field in a host material. Thus, the emission colour is well tunable by subtle changes in the chemical composition of the host compound, coordination number and symmetry of the site the divalent lanthanide occupies within a respective compound. Among the divalent lanthanides, Eu^{2+} has attracted a special interest due to the ease of its stabilization relative to the other divalent lanthanides and the fact that it shows emission within the visible range of the spectrum. In fact, due to these outstanding properties, modern functional materials are mainly based on hosts doped with Eu^{2+} ions. Eu^{2+} activated $\text{BaMgAl}_{10}\text{O}_{17}$ (BAM) is, for instance, the blue component in discharge lamps mentioned above [3]. For LEDs, several Si-based nitrides such as $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ [9] or $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M = Sr, Ba) are already in use [10–12]. Dorenbos [13] provided a review of all Eu^{2+} doped host materials up to the last 10 years.

* Corresponding author.
E-mail address: wurland@arcor.de (W. Urland).

Table 1

Electrostatic and spin-orbit coupling parameters for the free Eu^{2+} ion. Values are obtained from a least square fit of the lowest energy levels, obtained from the NIST database [32].

Slater-Condon parameters cm^{-1}		Spin-orbit coupling constants cm^{-1}		
ff Interaction		fd Interaction		
F_2	494.4	F_2	136.3	
F_4	29.8	F_4	7.0	$\xi(4f)$ 1332
F_6	5.4	G_1	180.5	$\xi(5d)$ 1092
		G_3	28.3	
		G_5	2.8	

The photoluminescence structure relationship of Eu^{2+} ions is, however, also interesting from a fundamental perspective, which is extremely important for the predictability and thus the selective design of novel luminescent materials. However, it is by far not understood in detail and thus, also requires attention. For instance, the impact of covalent character of the Eu ligand bond upon the energetic position of the 5d levels is a well-known fact that can be used to influence the appearance of an efficient broad banded $[\text{Xe}]4f^65d^1 \rightarrow [\text{Xe}]4f^7$ or $[\text{Xe}]4f^7 \rightarrow [\text{Xe}]4f^7$ sharp line emission of Eu^{2+} . This has been impressively shown in highly ionic compounds like $\text{MAIF}_5:\text{Eu}^{2+}$ ($M = \text{Sr}, \text{Ba}$) [14] or $\text{AMgF}_3:\text{Eu}^{2+}$ ($A = \text{K}, \text{Rb}$) [15,16], in which $[\text{Xe}]4f^7 \rightarrow [\text{Xe}]4f^7$ luminescence of Eu^{2+} was observed at low temperatures and $[\text{Xe}]4f^65d^1 \rightarrow [\text{Xe}]4f^7$ emission could be induced by thermal activation. Moreover, in a recent work, Suta et al. [17] have studied the photoluminescence properties of $\text{CsMBr}_3:\text{Eu}^{2+}$ ($M = \text{Mg}, \text{Ca}, \text{Sr}$), where Eu^{2+} occupies the M^{2+} sites coordinated by 6 Br^- ions with an approximate O_h symmetry. They have found that the emission colour evolves from green for $M = \text{Mg}$ to blue for $M = \text{Ca}$ and to violet for $M = \text{Sr}$ due to the decreasing Eu-Br distances during this series. An interesting fact in these compounds is the presence of a highly resolved fine structure in the excitation spectra that normally arises when the exchange interaction between the $[\text{Xe}]4f^6$ configuration and the 5d electron is very low [18]. This observation makes them extremely suitable for computational approaches and allows experimental verifications of theory.

There have already been several attempts to theoretically treat $[\text{Xe}]4f^m \rightarrow [\text{Xe}]4f^{m-1}5d^1$ transitions. For the trivalent lanthanides, semi-empirical methods have been reported which allow good simulations of the experimental spectra based on crystal field theory and the inclusion of symmetry [19–21]. For the divalent lanthanides, however, such calculations are only sparingly reported. CsCaBr_3 is an ideal compound for testing novel theoretical approaches in this area since it crystallizes in a perfect perovskite structure and the high symmetry simplifies the spectra and calculations significantly. Recently, there have been several attempts to theoretically predict the appearance of the absorption and emission spectra of Yb^{2+} in CsCaBr_3 based on ab-initio model potentials under inclusion of spin-orbit coupling [22–24]. Yb^{2+} is, however, a relatively simple case due to the presence of only 140 microstates for the $[\text{Xe}]4f^{13}5d^1$ excited configuration and also much less suitable for applications. It would therefore be satisfying to develop theoretical methods for other divalent lanthanides, especially Eu^{2+} , with higher total degeneracies as well. Our group has been a pioneer in the description of the $[\text{Xe}]4f^m$ and $[\text{Xe}]4f^{m-1}5d^1$ multiplet energy levels involved in the light emitting transitions within a ligand field theory framework [25–27]. These computational calculations are very important, not only because they are a cheaper alternative to experimental work in the search and design of new functional materials, but also because they allow gaining a deeper insight in the behaviour of a given system that allows predictions and therefore a tailoring of optical materials.

Here we present our methodology to calculate the excitation spectrum of Eu^{2+} doped compounds with ligand field theory taking $\text{CsCaBr}_3:\text{Eu}^{2+}$ as an example.

2. Theoretical model

The Hamiltonian operator of a lanthanide ion embedded in a host lattice can be described as:

$$H = H_{EE} + H_{LF} + H_{SO} \quad (1)$$

where H_{EE} represents the electron-electron Hamiltonian contributing to the electrostatic repulsion and exchange effects, H_{LF} is the ligand field perturbation on the central ion and H_{SO} represents the spin-orbit coupling. These operators are in principle written in the basis of all the Slater determinants, which are $\binom{14}{7} = 3432$ -fold for the $[\text{Xe}]4f^7$ manifold and $\binom{14}{6} \cdot \binom{10}{1} = 30,030$ -fold dimensional for the $[\text{Xe}]4f^65d^1$ manifold in the case of Eu^{2+} . The diagonalization of such huge matrices requires an extraordinary amount of computational time and effort. Therefore, the problem cannot be approached in brute force manner. However, a rational simplification is to limit on the octet states, as discussed in the following paragraph.

For f electrons, the electrostatic term dominates over spin-orbit coupling and the ligand field. Therefore, the ground state of the $[\text{Xe}]4f^7$ configuration is mainly an 8S term according to Hund's rules. Only transitions from this state to other octets are spin-allowed, which will give the main contribution to the intensity. Therefore, in order to reproduce the behaviour of absorption experiments, it is sufficient to consider the following eigenstates of H_{EE} :

$$[\text{Xe}]4f^7: ^8S \quad (2)$$

$$[\text{Xe}]4f^65d^1 : ^8P + ^8D + ^8F + ^8G + ^8H \quad (3)$$

This reduces the number of basis microstates to only 288 (8 from the $[\text{Xe}]4f^7$ and 280 from the $[\text{Xe}]4f^65d^1$ configuration) and, including a high symmetry, retains many of the degeneracies. This makes the calculations much more feasible.

H_{EE} is a two electron term that can be expressed in the basis of the Slater-Condon parameters [28,29]. They include the parameters for the direct coulomb interaction for the 4f shell, $F_k(\text{ff})$ ($k = 0, 2, 4, 6$), and the inter-shell parameters, $F_k(\text{fd})$ ($k = 0, 2, 4$). Moreover, the parameter denoting the exchange interaction within the $[\text{Xe}]4f^65d^1$ configuration, $G_k(\text{fd})$ ($k = 1, 3, 5$), are included. $F_0(\text{ff})$ and $F_0(\text{fd})$ cannot be discriminated separately. It should be noted that $F_0(\text{ff})$ is the same for all $[\text{Xe}]4f^7$ terms and similarly, $F_0(\text{fd})$ does not contribute to the splitting of the terms of the excited configuration $[\text{Xe}]4f^65d^1$. They can be omitted by combining them with the h_d and h_f pure one electron energies of the terms into a parameterized energy denoted by ΔU_0 (see Eq. (4)), which represents the electrostatic splitting between the 8S term and the octet $[\text{Xe}]4f^65d^1$

Table 2

Values of the crystal field splitting, $10Dq$, the electrostatic splitting between the $[\text{Xe}]4f^7$ and the $[\text{Xe}]4f^65d^1$ octet manifolds, ΔU_0 and the nephelauxetic parameter β obtained by a fit to the excitation spectrum of Eu^{2+} in CsCaBr_3 (see Figure 1).

Fitted parameter	Value
$10Dq$	$11,542 \text{ cm}^{-1}$
ΔU_0	$37,640 \text{ cm}^{-1}$
β	0.748

manifolds:

$$\Delta U_0 = h_d - h_f + 6F_0(fd) - 6F_0(ff) + 60F_2(ff) + 198F_4(ff) + 1716F_6(ff) \quad (4)$$

The basis set of the model was obtained starting from configurations with highest S_z spin projection of each octet orbital state from the $[\text{Xe}]4f^7 + [\text{Xe}]4f^65d^1$ set and applying ladder operators to that projection for smaller S_z components, down to the $-S_z$ series. So, in principle the basis set has multi configuration elements.

H_{L_f} is a one electron term which, written in the basis of the seven 4f and five 5d orbitals, can give rise up to $(12 \cdot 13)/2 = 78$ different parameters. However, the symmetry of the system drastically reduces this value. In the case of O_h symmetry, and considering a perfect shielding of the 4f orbitals, the ligand field can be described by just one parameter, Dq , which is $1/10$ of the energy splitting between the t_{2g} and e_g one electron states of the 5d orbitals.

H_{SO} is also a one electron term, which can be expressed in terms of the two spin-orbit coupling constants $\xi(4f)$ and $\xi(5d)$ for the 4f and 5d orbitals, respectively.

Finally, the transition probabilities and thus, the observed intensities for transitions between the ground state and an excited state are determined by the following matrix element:

$$I \propto |\langle 5d | \vec{\mu} | 4f \rangle|^2 \quad (5)$$

where $\vec{\mu} = e \cdot \vec{r}$ is the electric dipole operator. It is noteworthy that, in fact, off diagonal 5d-4f matrix elements contribute to the transition intensities.

We have developed our own codes to calculate the energy values, eigenfunctions and transition probabilities based on these parameters, which can be executed within the Matlab [30] or, alternatively, in the Octave framework [31].

3. Results and discussion

We tested our method by trying to reproduce the excitation spectrum of Eu^{2+} doped into CsCaBr_3 [17], in which the Eu^{2+} ions occupy sites with perfect octahedral symmetry. In order to simplify our work, we started by calculating the Slater-Condon parameters and spin-orbit coupling constants from a fit of the lower energy states of the Eu^{2+} free ion [32] (see Table 1).

These parameters were used as starting point to calculate the electronic properties of Eu^{2+} in this host and only three new parameters were introduced to reproduce the effect of the ligands in the experimental result: $10Dq$, ΔU_0 and β . $10Dq$ represents the crystal field splitting of the 5d levels in O_h symmetry and ΔU_0 denotes the splitting between the $[\text{Xe}]4f^7$ and the $[\text{Xe}]4f^65d^1$ terms with octet multiplicity, as already mentioned in the section of the theoretical model. β is the nephelauxetic parameter, which is multiplied as a correction factor with the Slater-Condon parameters of the f-d interaction. It represents the reduction of the electrostatic interaction between the 4f electrons and the 5d electron due to the expansion of the 5d orbital towards the ligand orbitals and accordingly, the delocalization of the 5d electron into the ligand orbitals. The fitted parameters are shown in Table 2. We obtained a value for $10Dq$ of $11,542 \text{ cm}^{-1}$, in good agreement with the experimentally

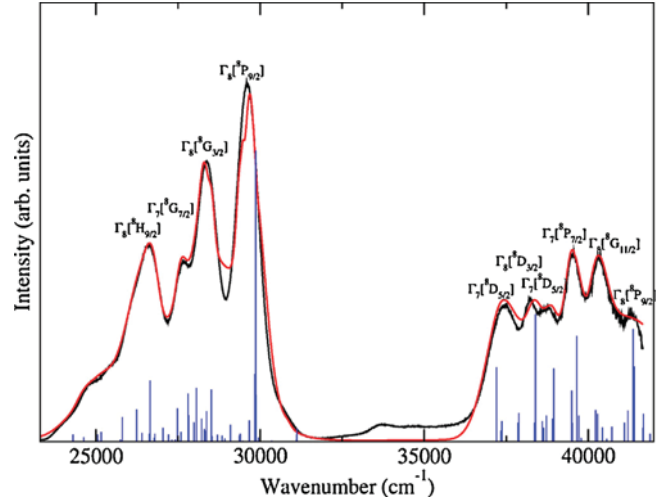


Figure 1. Calculated (red line) and experimental excitation spectra (black line, see [17]) of Eu^{2+} doped into CsCaBr_3 . Blue lines are used to indicate the multiplet energy levels and their transition probability. The irreducible representations of the states of the $[\text{Xe}]4f^65d^1$ configuration are also denoted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

proposed value of $12,700 \text{ cm}^{-1}$ [17]. The value of ΔU_0 also coincides nicely with the energy barycenters of the octet manifolds of the excited $[\text{Xe}]4f^65d^1$ configuration with a reported average value of $39,780 \text{ cm}^{-1}$ [33,34].

The nephelauxetic parameter β indicates a slightly covalent character of Eu^{2+} -Br bond that can be quantified by $k = 1 - \beta = 0.252$, i.e. the bond can be assumed to be roughly 25% covalent in character. This result should also be expected, since the Br^- ions are soft ligands according to the Pearson concept and therefore, a delocalization of the 5d electron of Eu^{2+} into the larger 4p orbitals of the Br^- ligands is plausible. Thus, the fitted parameters are acceptable from a qualitative physical perspective and in good agreement with experiment.

After having fitted the three parameters compiled in Table 2, we sought to compare our results with the experimental spectrum, as illustrated in Figure 1. The black line corresponds to the experimental results according to [17]. The blue lines represent the multiplet energy levels of the $[\text{Xe}]4f^65d^1$ manifold. Their height is proportional to the transition probability. A red line can be obtained after applying a Gaussian fit with the area under the curve being proportional to the transition probability of each energy value. The agreement with the experimental spectrum which corresponds to electron-vibrational transitions is remarkably good.

An advantage of our calculation is that it allows the assignment of the wave function of each spectroscopic term. In Figure 1, the irreducible representations of the terms with highest intensity contribution to each peak according to the octahedral double group O_h^* are denoted. This is in contrast to the common approach of using a decoupled scheme, which consists in assigning each fine structure peak within a broad $[\text{Xe}]4f^65d^1$ excitation band to a 7F_J energy level ($J=0-6$) arising due to coulomb and spin-orbit interactions within the $[\text{Xe}]4f^6$ core, whereas the broad envelopes are assigned to the 5d states t_{2g} and e_g split by the ligand field.

Finally, we attempted to provide a full energy level scheme of the different levels arising from the $[\text{Xe}]4f^65d^1$ excited configuration of Eu^{2+} . Figure 2 illustrates the systematic evolution and splitting of the different states after coulomb repulsion (H_{EE}), spin-orbit coupling (H_{SO}) and finally the splitting due to the symmetry of the ligand field (H_{LF}) having taken into account. It should be noted that due to the odd number of electrons the final states are at least two-fold degenerate and form Kramer's doublets (Γ_7) as well as quadruplets (Γ_8).

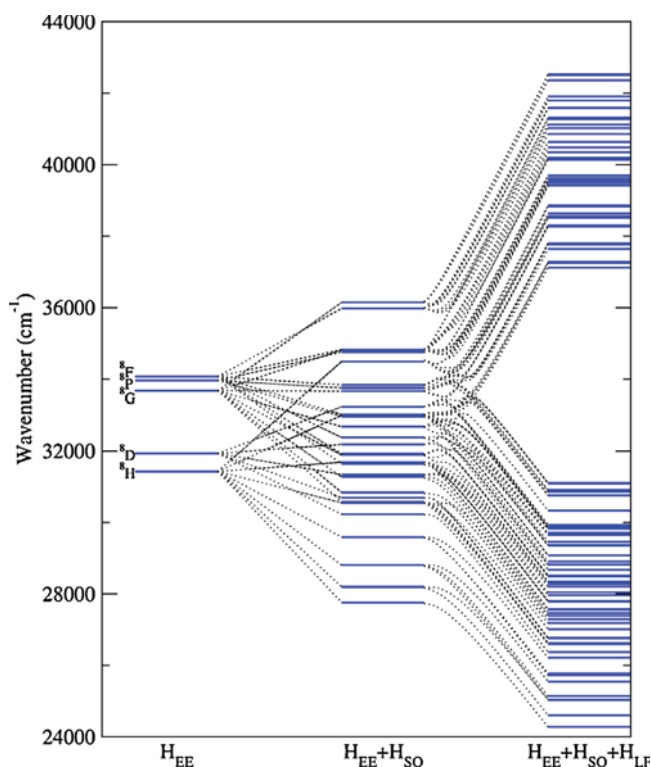


Figure 2. Evolution of the [Xe]4f⁶5d¹ multiplet energy levels when spin-orbit and ligand field contributions are progressively introduced into the Hamiltonian.

4. Conclusions

We have presented an accurate and reliable method for reproducing the excitation spectrum of Eu²⁺ activated CsCaBr₃. The agreement with the experimental spectrum as well as the deduced values thereof is excellent. Our full description of the Hamiltonian and of the wave functions of the different states allows us to unequivocally identify their corresponding irreducible representations in the double group. This provides a method to treat more complicated divalent lanthanides theoretically and could lead to the possibility of tailoring novel phosphors useful in applications in a cheap manner. In the future, this method can be combined with first principles calculations of the required parameters in order to predict luminescence spectra of other Eu²⁺ doped systems even with lower symmetry, which make them of ultimate interest in the future design of new phosphors.

Acknowledgements

This work was supported by the Swiss National Science Foundation and the State Secretariat for Research and Innovation. F. Cimpoesu also greatly acknowledges the grant PCE 14/2013 UEFIS-CDI from the Romanian Research Council.

References

- [1] S. Nakamura, G. Fasol, *The Blue Laser Diode*, Springer, Berlin, 1997.
- [2] N.C. Chang, J.B. Gruber, *J. Chem. Phys.* 41 (1964) 3227.
- [3] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem. Int. Ed.* 37 (1998) 3084.
- [4] B.R. Judd, *Phys. Rev.* 127 (1962) 750.
- [5] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511.
- [6] L. Smentek, *J. Phys. B: At. Mol. Opt. Phys.* 32 (1999) 593.
- [7] B.G. Wybourne, L. Smentek, *J. Alloys Compd.* 341 (2002) 71.
- [8] H.A. Höpfe, *Angew. Chem. Int. Ed.* 48 (2009) 3572.
- [9] V. Bachmann, T. Jüstel, A. Meijerink, C. Ronda, P.J. Schmidt, *J. Lumin.* 121 (2006) 441.
- [10] Y.Q. Li, et al., *J. Alloys Compd.* 417 (2006) 273.
- [11] X. Piao, T. Horikawa, H. Hanzawa, K.-I. Machida, *Appl. Phys. Lett.* 88 (2006) 161908-1.
- [12] H.A. Höpfe, H. Lutz, P. Morys, W. Schnick, A.J. Seilmeier, *Phys. Chem. Solids* 61 (2000) 2001.
- [13] P. Dorenbos, *J. Lumin.* 104 (2003) 239.
- [14] R.A. Hewes, M.V. Hoffman, *J. Lumin.* 3 (1971) 261.
- [15] D.K. Sardar, W.A. Sibley, R. Alcalá, *J. Lumin.* 27 (1982) 401.
- [16] A. Ellens, A. Meijerink, G. Blasse, *J. Lumin.* 59 (1994) 293.
- [17] M. Suta, P. Larsen, F. Lavoie-Cardinal, C. Wickleder, *J. Lumin.* 149 (2014) 35.
- [18] F.M. Ryan, W. Lehmann, D.W. Feldman, J. Murphy, *J. Electrochem. Soc.* 121 (1974) 1475.
- [19] L. van Pieterson, R.T. Wegh, A. Meijerink, M.F. Reid, *J. Chem. Phys.* 115 (2001) 9382.
- [20] L. van Pieterson, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, *Phys. Rev. B* 65 (2002) 045113-1.
- [21] L. van Pieterson, M.F. Reid, G.W. Burdick, A. Meijerink, *Phys. Rev. B* 65 (2002) 045114-1.
- [22] G. Sánchez-Sanz, L. Seijo, Z. Barandiarán, *J. Chem. Phys.* 131 (2009) 024505-1.
- [23] G. Sánchez-Sanz, L. Seijo, Z. Barandiarán, *J. Phys. Chem. A* 113 (2009) 12591.
- [24] A.J. Salkeld, M.F. Reid, J.-P.R. Wells, G. Sánchez-Sanz, L. Seijo, Z. Barandiarán, *J. Phys.: Condens. Matter* 25 (2013) 415504-1.
- [25] H. Ramanantoanina, W. Urland, F. Cimpoesu, C. Daul, *Phys. Chem. Chem. Phys.* 15 (33) (2013) 13902.
- [26] H. Ramanantoanina, W. Urland, A. García-Fuente, F. Cimpoesu, C. Daul, *Chem. Phys. Lett.* 588 (2013) 260.
- [27] H. Ramanantoanina, W. Urland, A. García-Fuente, F. Cimpoesu, C. Daul, *Phys. Chem. Chem. Phys.* 16 (2014) 14625.
- [28] J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, Cambridge, 1961.
- [29] S. Hüfner, *Optical Spectra of Transparent Rare Earth Compounds*, Academic Press, New York, 1978.
- [30] *MATLAB and Statistics Toolbox Release R2014a*, The MathWorks, Inc., Natick, MA, United States, 2014.
- [31] J.W. Eaton, D. Bateman, S. Hauberg, *GNU Octave Version 3.0.1 Manual: A High-level Interactive Language for Numerical Computations*, Create Space Independent Publishing Platform, 2009.
- [32] Kramida, A., Ralchenko, Y., Reader, J., NIST ASD Team, <http://physics.nist.gov/asd> (accessed 24.04.14).
- [33] J. Sugar, N. Spector, *J. Opt. Soc. Am.* 64 (1974) 1484.
- [34] P. Dorenbos, *J. Phys.: Condens. Matter* 15 (2003) 4797.