# Nonequivalent lanthanide defects: Energy level modeling

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## ARTICLE INFO

## ABSTRACT

Empirical charge-state transition level schemes are popular tools to model the properties of lanthanide-doped materials and their construction has become standard practice. Typically, it is implicitly assumed that all lanthanide ions form isostructural defects. However, in practice, multiple nonequivalent defects related to the same lanthanide can occur or different lanthanides can even incorporate in different ways. The consequences of these complications on the impurity energy levels are discussed in this article. It seems that small structural differences around the lanthanide dopant can give rise to important spectral differences in its emission. These are not always clearly reproduced by the charge-state transition level schemes. Improvements to the existing procedure are suggested and applied to the lanthanide ions in the well-studied host crystals $SrAl_2O_4$, $Sr_2Si_5N_8$ and $SrGa_2S_4$.

## 1. Introduction

Transparent inorganic solids have a long history of optical activation by crystallographic defects. Gems that are colored by metal impurities or color centers are well-known in mineralogy while optical materials based on intentionally doped dielectrics are integral parts of modern technologies such as lighting, electronic displays, medical imaging etc [1–6]. In these cases, the defects are mostly structurally simple point defects such as a missing atom, i.e. a vacancy, or an impurity atom in place of a normal atom, i.e. a substitutional defect [7]. In the following, defects which are induced by doping a crystal with lanthanide ions are considered.

Since the emergence of quantum mechanical theories, spectroscopy has been associated with energy level schemes, representing a connection between the experimental observables, i.e. the spectra, and the fundamental interactions. For this reason, understanding the physical origin of the luminescence behavior of a particular material often boils down to constructing an energy levels scheme. The distinct energy levels are suitably labeled, encoding for the dominant interactions. Furthermore, selection rules and transition probabilities are governed by the interaction of the physical system with the ambient electromagnetic field, i.e. incident photons.

Two important classes of energy level schemes exist [8]. Firstly, there are many-body schemes in which the energy level represents the total energy of the complete system. This means that not only the electrons which are considered as spectroscopically active are included, but also the other electrons and nuclei of the system. Formally, spectroscopic transitions can only be correctly described in a many-body framework. This is especially true in the case of transition metal or lanthanide ions due to the important electron correlations in these systems, i.e. all electrons of the system are to a certain extent affected by the excitation [9]. Secondly, in single particle energy level schemes, individual electrons are assigned to individual (spin)orbitals. In some systems, a single (quasi)particle picture is able to describe the electronic structure, yielding single particle states that are either occupied or empty. An example are the valence and conduction bands of a semiconductor [10].

In order to avoid the need of the explicit calculation of the electronic structure and optical properties of these materials, trends have been described, yielding not only predictability, but also empirical energy level schemes [11]. The nature of the empirical energy level schemes under discussion requires some attention as they should be envisioned as a separate tool with respect to the above-mentioned single-particle or many-body energy level schemes. Essentially, a single-particle picture of the host material, i.e. the valence and conduction bands, are utilized and impurity levels of the lanthanide are *defined* as so-called charge-state transition levels. These correspond to the value of the electronic chemical potential at which the formal charge of the lanthanide ion changes [12]. The exact meaning of the empirical

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energy levels is further elucidated in Ref. [8].

Lanthanide ions show a particular electronic structure. The incompletely filled 4f shell is effectively screened by the environment by filled 5s and 5p shells. Furthermore, some lanthanide ions show a low-lying $4f^{N-1}5d^1$ excited configuration, allowing efficient excitation with visible or near ultraviolet light. These particular features give rise to a systematic behavior of the ionization potentials and 4f-5d excitation energies across the lanthanide series which can be exploited to devise empirical rules with predictive power. This was pioneered by Thiel in the context of photoelectron spectroscopy and further developed by Dorenbos, mostly based on optical spectroscopy [13–15,11]. The uncertainties associated with these empirical models and the accuracy by which experimental quantities can be predicted have recently been addressed in detail [8].

Up to now, the described empirical rules and techniques for constructing charge-state transition level schemes have been applied to many host materials [16–23]. This can be unambiguously done for host materials in which all lanthanides act identically in chemical and crystallographic terms. One can expect that often this is true because of their similar ionic radii and chemical behavior. However examples are known where this is not the case. Furthermore, there is a one-to-one correspondence between the number of nonequivalent defects in a certain host and the number of charge-state transition levels for a dopant. If multiple defect geometries for the same foreign atom are possible, multiple energy level schemes are necessary for a correct description. Both these subtleties are often neglected or simply forgotten.

In this work, the empirical energy level models are applied to lanthanide-doped materials with more challenging host compounds, featuring multiple nonequivalent lattice sites on which the lanthanides can incorporate. $SrAl_2O_4$ and $Sr_2Si_5N_8$ are presented as case studies. Site-selective spectroscopy can offer a tidy opportunity to separate the spectral features and construct charge-state transition schemes for the different defect geometries. Remaining difficulties such as correlating the spectral features to the defects are discussed.

In the second part of this article, recent work on the lanthanide doped ternary sulfide $SrGa_2S_4$ is presented. It is known that the first coordination shell is severely altered when $Ce^{3+}$ is incorporated [24], yielding a completely different situation than for $Eu^{2+}$ doping. In this case, the use of empirical rules that relate spectral properties of different lanthanides becomes severely restricted. The repercussions on the construction of charge-state transition level schemes are discussed in detail.

## 2. Experimental

In this manuscript, lanthanide defects are described in three host materials, i.e. $SrAl_2O_4$, $Sr_2Si_5N_8$ and $SrGa_2S_4$. The discussion of the former two is based on literature data, the discussion of the latter is based on following experiments.

$SrGa_2S_4$:$Ln^{Q+}$ powders were synthesized by a solid state reaction at high temperature (2 h at 900°C, heating rate of 7.5 °C/min) under a flow of forming gas (90% $N_2$, 10% $H_2$) with SrS (Alfa Aesar, 99.9%) and $Ga_2S_3$ (Alfa Aesar, 99.99%) as starting materials for the host crystal and lanthanide fluorides ($LnF_3$, all at least 99.5% pure) as source of the dopants. The selected dopants are Ce, Pr, Sm, Eu, Tb and Tm. A doping concentration of 1 mol% was used for all syntheses.

The phase purity of the obtained powders was verified by means of X-ray diffraction (XRD) with Cu$K\alpha_1$ radiation on a Bruker D5000 diffractometer (40 kV, 40 mA).

Luminescence emission and excitation spectra were measured with an Edinburgh FS920 fluorescence spectrometer. Spectra at low temperature were obtained by using an Oxford Optistat CF cryostat.

Diffuse reflectance spectra were measured with a Varian Cary 500 spectrophotometer, equipped with an internal integrating sphere, using $BaSO_4$ as a reference. From the reflectance spectra, the square of the Kubelka-Munk function was calculated and fitted with a straight line to obtain an estimate for the optical band gap.

## 3. Results and discussion

### 3.1. Multiple nonequivalent lanthanide defects

In this paragraph, two examples of host compounds ($SrAl_2O_4$ and $Sr_2Si_5N_8$) are discussed which feature two nonequivalent substitutional defects upon lanthanide doping (see Fig. 3). This poses additional difficulties when the electronic structure is empirically assessed as both lanthanide defects require a separate energy level scheme. Examples are included for which the occurrence of the nonequivalent defects is clear from the optical spectra, i.e. site-selective spectroscopy can be performed. This is preferably done on low concentrated systems, avoiding interactions between nonequivalent defect centers. Interactions between centers result in energy transfer which can obscure the optical spectra.

Site-selective spectroscopy of the $Ce^{3+}$ ion is an important first step as it allows to construct vacuum referred binding energy level schemes for the 4f levels. This is thanks to an empirical rule due to Dorenbos, relating the centroid shift of the $Ce^{3+}$ $5d^1$ manifold to the vacuum referred binding energies (VRBE) of all lanthanides [25,26]. This procedure, in which the empirical Coulomb correlation energy is used as intermediate parameter is described in two review papers [11,8]. In this way, the 4f ionization potentials of the different lanthanide defects are obtained with a reasonable accuracy [8].

Next, the host compound's valence and conduction band need to be added to obtain a complete charge-state transition level diagram and the host referred binding energies (HRBE). From photoluminescence excitation spectroscopy of a trivalent lanthanide, the anion to lanthanide charge-transfer (CT) energy can be obtained, approximately probing the 2+/3+ charge-state transition level. The binding energy difference between two nonequivalent $Ln^{3+}$ defects is significantly smaller than the typical width of a charge-transfer spectral band [27]. As the ionization potentials for both defects were already calculated, deconvolution of the CT band poses no additional problems.

#### 3.1.1. $SrAl_2O_4$

Doped with divalent europium, strontium aluminate ($SrAl_2O_4$) features an extensively studied green afterglow which can be intensified upon codoping with trivalent dysprosium [28–30]. Interestingly, when this material is cooled below 250 K, a second emission band emerges in the blue spectral region [31]. The origin of this band has been the debated since it was first found. Although an explanation in terms of incorporation of $Eu^{2+}$ on the two nonequivalent lattice sites seems the most simple one, it was plead that the minor geometrical differences between the Sr1 and Sr2 sites cannot account for the differences between the two spectral features [32–35]. Alternatively, more exotic explanations such as alignment of Eu ions, hole release or even emission from a higher $4f^65d^1$ multiplet were contrived [32,34,35].

Recently, empirical rules, relating the bond lengths of the undistorted lattice sites to the multiplet structure of the excited $4f^65d^1$ configuration were applied, showing that the order of magnitude of the spectral differences between the blue and green emission bands can be perfectly explained by the structural differences between both lattice sites, discarding the more exotic explanations for the occurrence of two emission bands [31].

Also upon $Ce^{3+}$ doping, it was spectroscopically shown that two