

# An alternative description for the interaction between the $\text{Eu}^{3+}$ ion and its nearest neighbours



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## ABSTRACT

The  $\text{LiYF}_4:\text{Eu}^{3+}$  and the  $\text{Eu}(\text{btf}_a)_3(4,4\text{-bipy})(\text{EtOH})$  compounds are being revisited by the method of equivalent nearest neighbours (MENNs) and the simple overlap model, this time to suggest a comparison between: the europium local symmetry in complexes containing  $\beta$ -diketones and the  $S_4$  symmetry in the  $\text{LiYF}_4:\text{Eu}^{3+}$ ; and the ionic bonding in lanthanide containing compounds as pure electrostatic attraction. The  ${}^7F_1$  level splitting was satisfactorily predicted in both cases by very similar sets of charge factors. This similarity indicates that the lanthanide ion treats the chemical species (N, O and F) in its first neighbourhood merely as negative charges.

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## 1. Introduction

The lanthanide ion-nearest neighbours (Ln-NN) interaction has been a subject of experimental and theoretical discussions, mainly due to the need of development of new materials to be used in optical devices. From the crystal field point of view, the number of lines of each  ${}^5D_0 \rightarrow {}^7F_j$  transition in the spectra of systems doped with trivalent europium ions ( $\text{Eu}^{3+}$ ) is almost an unambiguous way of analysing its local symmetry group [1,2]. The electrostatic neutrality, which is a requirement to ensure the stability of a solid, and the local symmetry have been used by the method of equivalent nearest neighbours (MENNs) to predict the Eu-NN charge of interaction and the  ${}^7F_1$  energy level splitting ( $\Delta E$ ) [3,4]. The MENN is based on the simple overlap model (SOM, [5]) and the level splitting is predicted by the Auzel–Malta expression, which describes the maximum splitting of any multiplet of any trivalent lanthanide ions as a function of the crystal field strength parameter,  $N_V$  [6].

Even though good predictions have been achieved with the MENN, some specific point concerning the magnitude of the charge factors and the local symmetry still remain obscure. For instance, the spectra of Eu-complexes involving  $\beta$ -diketones present the same profile of the  ${}^7F_1$  energy sublevels [7–12], and similar to that observed in the  $\text{LiYF}_4:\text{Eu}^{3+}$  crystal [13]. As the number of lines of the  ${}^7F_1$  level is the starting point to determine the local symmetry of the  $\text{Eu}^{3+}$  ion, one can suggest that the luminescent ion in these compounds have approximately the same local symmetry.

However, the NN in the  $\text{LiYF}_4:\text{Eu}^{3+}$  crystal ([4]) and the  $\text{Eu}(\text{btf}_a)_3(4,4\text{-bipy})(\text{EtOH})$  complex (EuBTFA) [14] are not of the same chemical species. In the former, one has only  $\text{F}^-$  ions and in the latter  $\text{O}^{2-}$  and  $\text{N}^{3-}$  ions. In this work these systems are being revisited in order to present an alternative description for the interaction between the  $\text{Eu}^{3+}$  ion and its nearest neighbours.

## 2. Theory

In this study there are no changes in any model related to the crystal field theory. For details about the SOM and the Auzel–Malta model, it is suggested to the interested reader the following Refs. [5,6,15].

The MENN follows three constraints: (i) equivalent NN should be identified through the local symmetry; (ii) using the Auzel–Malta expression for the  ${}^7F_1$  level splitting (in which only crystal field parameters (CFP) with  $k = 2$  are operative), the  $\Delta E$  should be predicted by a set of charge factors,  $g_j$  ( $j$  running over the NN) ([4,6]); and (iii) the  $\sum_j g_j = 3$ , the valence of the central ion, in order to guarantee the local electrical neutrality. In constraint (i), when a symmetry operation displaces one NN to the position of another NN, these neighbours are equivalent and should have the same  $g_j$ . In this way, there is a reduction of degrees of freedom. The  $g_j$  are actually the unknowns (not parameters) of the MENN. Further, the reader should realise that the constraints (ii) and (iii) give rise to two equations, which consider the symmetry and electrostatic neutrality of the local site as the most important aspect for the present predictions. Therefore, the maximum value of  $c$ , the equivalence number of the MENN, must be 2. This is the reason why only sites with high

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symmetry are being analysed. This is an uncomfortable limitation of the method. In order to expand its applicability, a study involving the energy matrix of the  ${}^7F_j$  levels is being developed.

### 3. Results and discussions

In the  $\text{LiYF}_4:\text{Eu}^{3+}$  crystal the europium ion occupies a  $S_4$  symmetry, in which one can find two groups of four NN, each one with the same Eu–NN distance [15]. In a previous paper, the EuBTFA was studied and the  $\text{Eu}^{3+}$  ion was treated as occupying a  $C_1$  point symmetry (Fig. 1a) [3]. The main reason was the presence of the nitrogen ion as a NN and the chemical similarity was treated as an important feature for the equivalence and the nitrogen ion was assumed to be on the main axis of symmetry. Here, a new point of view is being assumed: independently of the chemical similarity of the NN and based on fundamental quantum mechanics, one has calculated the main axis of symmetry, defined by the axis of maximum moment of inertia (between the O4 and O6 ions, Fig. 1b). Thus, the nitrogen ion is being treated as equivalent to an oxygen ion. From the NN spherical coordinates (Table 1 and Fig. 1b) it is clear that one has a slightly distorted  $S_4$  symmetry, indeed. The choice of a  $S_4$  symmetry is due to the fact that the right local symmetry of the europium ion in the  $\text{LiYF}_4:\text{Eu}^{3+}$  is  $S_4$  and is approximate in the case of the complex. The use of the higher  $D_{2d}$  symmetry would be a unnecessary further approximation [16,17]. Then, two groups of equivalent NN are identified: O1–O4–O6–N1 ions and O2–O3–O5–O7 ions. In this way, constraints (ii) and (iii) constitute a consistent system of two equations and two unknowns (Eqs. (3) and (4) of [4]) exactly solved for both compounds.

Table 2 shows the sets of charge factors, the set of CFP, and  ${}^7F_1$  level splitting for the studied systems. Only the experimental  $\Delta E$  is written, because it has been reproduced exactly. Furthermore, one can note that the set of charge factors of the EuBTFA is comparable to that of the Eu-crystal. For the sake of comparison, the interested reader is encouraged to consult the charge factors of the Eu-complex considering the  $C_1$  site symmetry [3].

Some points deserve comments:

- (1) By taking into account that the ionic radius of the  $\text{Eu}^{3+}$  ion is always smaller than the divalent oxygen ion no matter the coordination number [18], only the minus signal in the  $\beta$  expression of the SOM has been applied [5];
- (2) For the  $\text{LiYF}_4:\text{Eu}^{3+}$  crystal the  $g_j$  versus  $R_j$  has shown a growing linear behaviour. For the EuBTFA complex, one has to deal with average distances, because all Eu–NN distances

**Table 1**

Crystallographic spherical coordinates and equivalent charge factors of NN of  $\text{Eu}^{3+}$  in EuBTFA [14].

|    | $R$   | $\theta$ | $\varphi$ | $g$   |
|----|-------|----------|-----------|-------|
| O1 | 2.417 | 138.57   | −39.34    | $g_2$ |
| O2 | 2.338 | 68.58    | −44.10    | $g_1$ |
| O3 | 2.322 | 106.48   | 44.64     | $g_1$ |
| O4 | 2.434 | 36.40    | 44.56     | $g_2$ |
| O5 | 2.384 | 108.46   | −140.39   | $g_1$ |
| O6 | 2.356 | 37.83    | −135.44   | $g_2$ |
| O7 | 2.443 | 73.04    | 128.57    | $g_1$ |
| N1 | 2.591 | 145.49   | 130.62    | $g_2$ |

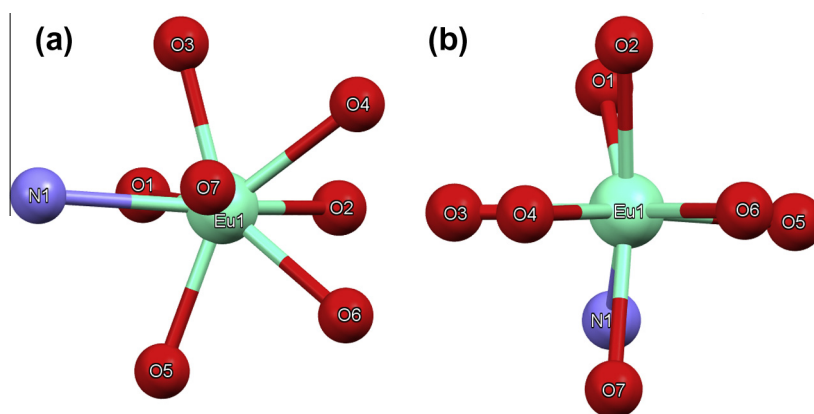
**Table 2**

Charge factor and  $B_q^2$  ( $\text{cm}^{-1}$ ) that reproduce the experimental splitting.

|                                | $g_1$    | $g_2$    | $B_0^2$ | $B_1^2$     | $B_2^2$      | $\Delta E$ |
|--------------------------------|----------|----------|---------|-------------|--------------|------------|
| EuBTFA (dist. $S_4$ )          | 0.257(4) | 0.493(4) | 598(9)  | 137i<br>(9) | −197i<br>(9) | 197        |
| Eu:LiYF <sub>4</sub> ( $S_4$ ) | 0.265(4) | 0.485(4) | 401(2)  | 0           | 0            | 96         |

are different. As in the crystal, the  $g_j$  versus  $R_j$  growing linear behaviour has been predicted:  $g_1$  ( $g_2$ ) is related to  $R_1 = 2.372\text{\AA}$  ( $R_2 = 2.450\text{\AA}$ );

- (3) When the  ${}^7F_1$  level splits in two lines one of them is degenerate. The negative (positive) signal of the  $B_0^2$  parameter defines that the lower line is single (doubly degenerate). In the crystal (complex) case the ground sub-level is degenerate (slightly non-degenerate). This has been correctly predicted in both cases, because  $B_0^2$  is positive (Table 2). For the complex, the influence of the CFP with  $q = 1$  on the crystal field strength parameter ( $N_V$ , [6]) is negligible and the small magnitude of the  $B_2^2$  parameter reflects the small splitting of the slightly non-degenerate sub-levels. Moreover, in both cases the splitting of  ${}^7F_1$  energy level is below of  $350\text{ cm}^{-1}$ , indicating that both compounds present a high symmetry [19]. This is another feature which confirms the assumption that the  $S_4$  site symmetry of the europium ion is slightly distorted. Indeed, as the Auzel–Malta equation for the  $\Delta E$  depends on the square of  $g_j$ , one has two possible sets of charge factors. The choice should be the solution which leads to the right  $B_0^2$  signal; and
- (4) The similarity between the sets of charge factors indicates that the europium positive ion feels its neighbourhood as an amount of negative charge, regardless the chemical species of the NN. One has then a good example to show that the ionic bonding is mainly an electrostatic attraction. This is also related to the shielding of the  $4f$  electrons.



**Fig. 1.** (a)  $C_1$  site symmetry and (b) slightly distorted  $S_4$  site symmetry of the  $\text{Eu}^{3+}$  ion in the EuBTFA [15].

Even though the sets of  $g_j$  solutions have been satisfactorily used to predict the magnitude and signal of the  $B_0^2$  parameter, then the  ${}^7F_1$  level splitting, the  $B_q^4$  and  $B_q^6$  parameters are not satisfactorily predicted. Consequently, the predictions of the splitting of other levels are not good. This failure of the MENN is being analysed.

#### 4. Conclusions

The method of equivalent nearest neighbours (MENNs) was applied to two europium doped systems, namely, the  $\text{LiYF}_4\text{:Eu}^{3+}$  crystal and the  $\text{Eu}(\text{btfa})_3(4,4\text{-bipy})(\text{EtOH})$  complex. These systems are being revisited, now to discuss the energy level splitting of the europium ion when interacting with different chemical species, whereas occupying approximately the same local symmetry. The signal of the  $B_0^2$  parameter and the  ${}^7F_1$  energy level splitting was predicted correctly in both cases. The sets of charge factors were calculated with no ambiguity and are very similar to each other. Such similarity confirms the assumption that the symmetry of the europium site is a  $S_4$  slightly distorted and that the europium ion attracts an amount of negative charge, just to neutralise its own site. This is a strong indication that the europium ion treats its neighbourhood as unnamed negative charges, independently of the chemical species there. This is truly an example to attest that the ionic bonding is mainly an electrostatic attraction. At this moment, only the  $\text{Eu}^{3+}$  ion in high symmetry sites can be analysed, because the method deals with just two equations. This seems to be the main MENN's limitation. One needs to include additional energy equations and apply the method to several other systems and to make the method more general.

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