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Theoretical investigation of the 7F_1 level splitting in a series of Eu^{3+} doped oxides matrixes

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Abstract

The point charge electrostatic model (PCEM) and the simple overlap model (SOM) are applied to a series of oxide crystals (Gd_2O_3 , Y_2O_3 , Lu_2O_3 , In_2O_3 and Sc_2O_3) and a silicate glass (Al_2O_3 – SiO_2) doped with the Eu^{3+} ion. The SOM factor $\rho(2\beta)^{k+1}$ is input as the shielding factor for all B_q^k expressions, which enters in the calculations of the crystal-field strength parameter, N_V . The maximum splitting ΔE of the 7F_1 manifold of the Eu^{3+} ion is then obtained as a function of N_V . It has been developed another way to calculate alpha, which is an expansion factor in the ΔE expression. For the glass, as the mean metal-ligating ions distances are larger than for the crystals, N_V and ΔE are smaller, as expected. The prediction of the PCEM shows a linear dependence between ΔE and N_V , even though the known mismatch in respect to the experimental splitting is kept. In the case of the SOM, two situations have been analyzed: firstly the charge factor varies in order to reproduce the experimental splitting (a phenomenological procedure); secondly the charge factor is the valence of the oxygen ions. The agreement between the experimental results and theoretical predictions for all investigated systems is very satisfactory in respect to both the linearity between ΔE and N_V and the ΔE splitting.

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1. Introduction

The effect of the nearest neighbors on the optical behavior of lanthanide (Ln^{3+}) system is firstly discussed by defining the interaction between the neighbors through the potential energy as a function of crystal-field parameters (CFP) [1]. These CFP are functions of charge factors and spherical coordinates of the ligating ions in respect to the central metal ion. The good agreement between X-ray measurements and the simulated structure of solid-state host (crystals, glasses, complexes) brings up the idea of predicting laser crystals as well as highly luminescent systems. The

confidence of such simulation procedures depends on what properties the simulated structures could fit [2–7].

In particular, the energy level splitting of Ln^{3+} ions is an interesting way of testing crystal-field parameter models, because the splitting depends on the local symmetry, i.e., the way the electric field of the first neighbors acts on the luminescent site [8–11].

In this work the splitting of the 7F_1 manifold (ΔE) of the Eu^{3+} ion is studied in a series of oxide systems (M_2O_3 crystals, $M = \text{Gd}, \text{Y}, \text{Lu}, \text{In}, \text{Sc}$ [12], and in the Al_2O_3 – SiO_2 glass [13]). The glassy structure is obtained after molecular dynamics simulation. The scalar crystal-field strength parameter [10,11] is obtained using the very well known point charge electrostatic model (PCEM) and the simple overlap model (SOM) [14], in order to explicit that the SOM alters the PCEM predictions in the right sense. The Ref. [15] is revisited in order to corroborate the importance

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of phenomenological crystal-field calculations [16]. For the first time a purely theoretical calculation is developed to confirm the linearity of ΔE versus N_V and the simulated glassy structure is used in this kind of calculation.

2. Theory

Based on the rotational invariance of the scalar crystal-field strength parameter, N_V , a model for the degeneracy lift of Ln^{3+} ions was developed [10]. The main idea in Ref. [10] is to give a more consistent meaning for the CFP. The maximum splitting of the Ln^{3+} manifold, ΔE , as a function of N_V is then obtained as follows:

$$\Delta E = \left[\frac{3g^2}{g(g+2)(g_a+1)\pi} \right]^{1/2} \left[\prod_k \left| \left\langle J \left\| \sum_i C^{(k)}(i) \right\| J \right\rangle \right| \right]^{1/3} N_V \quad (1)$$

In Eq. (1) g is the total degeneracy of the level and g_a is the degeneracy effectively removed. $C^{(k)}(i)$ is the Racah spherical tensor ($k = 2, 4, 6$, and i runs over the electrons of the central ion) and J is the total angular momentum associated to the level under investigation.

This complete expression is simplified in the case of discussing the Stark splitting of levels with small J values (say, $J = 1$ or $3/2$), because only $k = 2$ is to be taken [15].

$$\Delta E = \left[\frac{g_a \left| \left\langle J \left\| \sum_i C^{(2)}(i) \right\| J \right\rangle \right|^2}{g(\alpha^2 + 2)\pi} \right]^{1/2} N_V \quad (2)$$

For the case of $J = 1$ (the present case), $\alpha = 2(E_{>} - E_a)/\Delta E$ (Eq. (7) of the Ref. [15]). $E_{>}$ is the upper sublevel, E_a is the intermediary sublevel and $E_{<}$ is the lower sublevel. Here α is obtained after the following considerations: the root-mean-square deviation $(\Delta\epsilon)^2$ of a g -fold degenerate level can be expanded in units of the half the maximum splitting of the level [10]. For $J = 1$ one has

$$(\Delta\epsilon)^2 = \Delta E(2 + \alpha^2)/2g_a \quad (3)$$

But the rms is defined by

$$(\Delta\epsilon)^2 = [(E_b - E_{>})^2 + (E_b - E_a)^2 + (E_b - E_{<})^2]/g_a \quad (4)$$

E_b is the barycenter of the energy level. Assuming a symmetric repartition of levels, which is reasonable in the series of oxides studied in this work, $E_a - E_b$ is negligible compared to the other two terms and the final expression for α is

$$\alpha = \pm \sqrt{2} \frac{E_b - (E_{<} + \frac{\Delta E}{2})}{\frac{\Delta E}{2}} \quad (5)$$

The choice of the sign depends on the position of the energy level barycenter, in order to have $0 < \alpha < 1$. The calculation of the crystal-field strength parameter N_V is developed using the PCEM and the SOM [14]. In the PCEM the interacting potential between the metal and

the media is obtained using the valence of the nearest ions, this charge being positioned in the nearest ion site. In the SOM:

- (i) the potential energy due to the presence of the first neighbors is produced by charges uniformly distributed in small regions around the middle Ln–O distance;
- (ii) the charge in these regions is $-\rho qe$, ρ is proportional to the overlap between the central and ligating ions wave functions.

This leads to

$$B_q^2(\text{SOM}) = \rho[2/(1 + \rho)]^3 B_q^2(\text{PCEM}) \quad (6)$$

$$N_V(k = 2, \text{SOM}) = \rho[2/(1 + \rho)]^3 N_V(k = 2, \text{PCEM}) \quad (7)$$

$$\text{with [3]} \quad \rho = \rho_0(R_0/R)^{3.5} \quad (8)$$

ρ_0 is 0.05, the maximum overlap [17], and R_0 is the smaller Ln–O distance.

Numerical simulations using the molecular dynamics technique have been performed in order to obtain the microscopic structure of an alumino-silicate glass. Simulations details are presented in a previous paper [13].

3. Results and discussion

The spherical coordinates of all oxide crystals were taken from Ref. [12]. In the case of the glass, one has dealt with and average of 72 different sites. For each site, the B_q^k and ΔE values were calculated. The charge factor which enter in the CFP expressions is 2, the valence of the oxygen ion, in the PCEM and there are two situations for the SOM: firstly the charge factor varies in order to reproduce the experimental splitting (a phenomenological procedure: Theo-Phen case); secondly the charge factor is the valence of the oxygen ion (Theo case).

The calculation of the ΔE using the PCEM is the first interesting result (Fig. 1). For the sake of comparison the ΔE experimental values were associated to the same N_V values. Quantitatively, there is a mismatch between the PCEM predictions and the experimental ${}^7\text{F}_1$ level splitting, but the behavior of ΔE as a function of the N_V is linear. The magnitude of the PCEM predictions is around three times stronger than the measurements. The Fig. 2 shows that this difference is satisfactorily suppressed by the SOM factor.

In the Fig. 2 all results of ΔE versus N_V after applying different methods are shown. The experimental and phenomenological results are from Ref. [15]. For the theoretical predictions (Theo curves) the spherical coordinates and valence of the oxygen ions were input in the N_V expressions. In the Theo-Phen case it is used the phenomenological charge factor. The linearity as well as the similarity in respect to the phenomenological results from the Ref. [15] can be readily noted. In the case of the glass, the result is in the lower side of the linear curve (black star), with a phe-

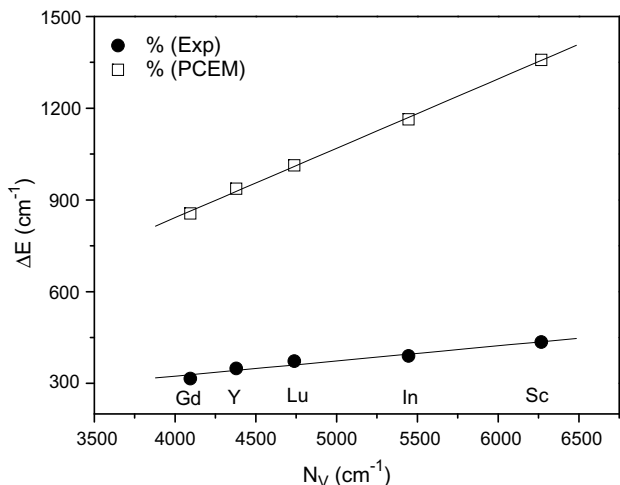


Fig. 1. ΔE as a function of N_V for both experimental and PCEM calculation. The lines are linear fit. For the sake of comparison, the experimental values of ΔE are associated to the N_V values from the PCEM predictions.

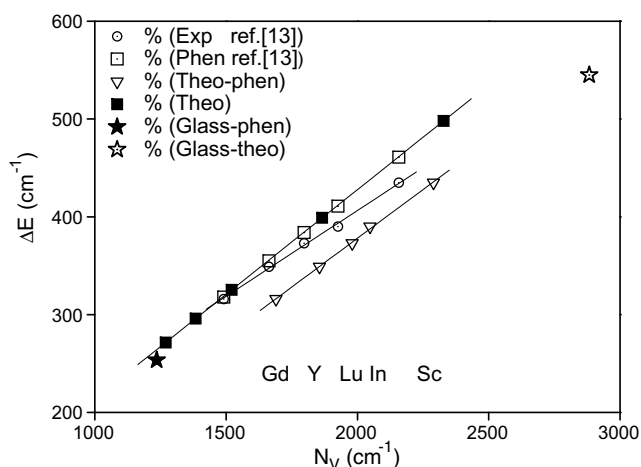


Fig. 2. ΔE as a function of N_V for experimental, theoretical and phenomenological calculations. The lines are linear fit. The experimental values of ΔE are associated to the N_V phenomenological values.

nomenological charge factor of 1.4. This is expected because the Ln–O distance is larger than in the oxides. However, when the valence of the oxygen is input as the charge factor, the prediction is not satisfactory at all (white star). This is the only mismatch in our calculations. The reason for this mismatch is being discussed in our group. For the series of oxides crystals, the charge factors varies as $1.7 < g < 2.4$.

At this point it is important to comment that in quantum chemistry calculations of the structure of europium complexes (e.g., Sparkle Model [5]), the value of the Mulliken charge is smaller than 1 in the most cases [2,7].

The linear behavior of g versus average Ln–O distance is shown in Fig. 3. This is physically acceptable, because the electronic repulsion is stronger the closer the interacting species are.

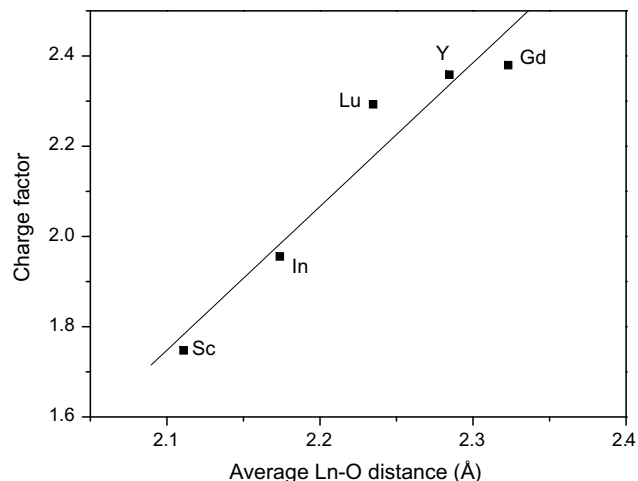


Fig. 3. Charge factor, g , of the oxide crystals as a function of the average distance Ln–O.

The linearity of ΔE versus N_V in both PCEM and SOM predictions is a very strong indication that B_q^k as well as N_V are as good as well defined physical concepts.

4. Conclusions

Oxide systems doped with Eu^{3+} ions were revisited through the point charge electrostatic model and simple overlap model, in order to discuss the ${}^7\text{F}_1$ level splitting as a function of the crystal-field strength parameter. The spherical coordinates that enter in the calculations were taken from X-ray data available in the literature for the crystals and from molecular dynamics simulation for the glass. The linear behavior of the ${}^7\text{F}_1$ manifold splitting as a function of the crystal-field strength parameter was reproduced even for the PCEM model and the SOM reproduces both linearity and magnitude. Then one can assert that both B_q^k and N_V are good and well defined physical quantities. The charge factor is a linear function of the average Ln–O distance, when the calculations were forced to reproduce the experimental ${}^7\text{F}_1$ level splitting. The range is $1.4 < g < 2.4$. It is not clear at this moment what this amount of charge could mean, even though it is physically acceptable that the interacting charge augments with the distance of the interacting atoms, because the electronic repulsion is smaller. For the first time the molecular dynamics simulation of glasses is used in this kind of investigation. Finally, excepted for purely theoretical results in the case of the glass, the good agreement between the predictions and experimental results certifies that theoretical calculations as well as phenomenological simulations are good tools for predicting optically active materials.

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