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The crystal field strength parameter and the maximum splitting of the 7F_1 manifold of the Eu^{3+} ion in oxides

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Abstract

We examine, from both the experimental and theoretical point of view, the behavior of the maximum splitting ΔE , of the 7F_1 manifold of the Eu^{3+} ion as a function of the so-called crystal field strength parameter, N_v , in a series of oxides. In connection with the original theory that describes the relation between ΔE and N_v , a more consistent procedure to describe this relation is presented for the cases of small total angular momentum J . Good agreement is found between theory and experiment.

Keywords: Crystal field splitting; Oxides

1. Introduction

The relation between the maximum splitting, due to a crystal field, of a ${}^{2S+1}L_J$ manifold of a rare earth ion and a rotational invariant, defined as the crystal field strength, was first established by Auzel in an empirical way [1]. Later on, this relation was justified on theoretical backgrounds [2]. The root-mean-square deviation of a number of levels belonging to a given manifold has also been expressed in terms of the so-called crystal field strength parameter [3,4]. An alternative set of rotational invariants has been defined in terms of the so-called intrinsic parameters which appear in the superposition model for the crystal field [5].

In obtaining the final expression that relates the maximum splitting of a J level to the crystal field strength parameter [2], the number of levels, $(2J+1)$ if J is integer and $(J+1/2)$ if J is half-integer, is

assumed to be large and their repartition is considered to be approximately homogeneous and proportional to an energy unit which is half the maximum splitting. When J is small, say equal to 1 or 3/2, a somewhat different procedure should be adopted. This is typically the case, for example, of the 7F_1 manifold of the Eu^{3+} ion.

Recently, it has been observed that the maximum splitting of the 7F_1 of the Eu^{3+} ions behaves in a way directly proportional to the crystal field strength parameter, with a coefficient of proportionality around 0.2 [6]. This is in qualitative agreement with the main theoretical results obtained in Ref. [2]. However, the theoretical prediction of this coefficient is a question that deserves to be discussed.

In the present paper we carry out a general discussion on the relation between the maximum splitting of a J level and the crystal field strength parameter for small J values. Attention will be focused on the case of the 7F_1 manifold of the Eu^{3+} ion. The evolution of its maximum splitting, as a function of the crystal field strength parameter, in a series of oxides doped with Eu^{3+} is then interpreted according to the theoretical results obtained.

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2. Experimental

2.1. Sample preparation and crystal structure

Polycrystalline samples of $M_{2-x}Eu_xO_3$, $x = 0.02$ and $M = Gd, Y, Lu, In$ and Sc , were prepared by coprecipitation of the oxalates. Stoichiometric proportions of the corresponding oxides were dissolved in diluted

HCl and coprecipitated with oxalic acid in excess. The precipitate was filtered and dried in a stove and subsequently calcinated at 1100°C . All samples contain 0.02% Eu^{3+} .

The sesquioxides crystallizes in the C-type rare earth oxide structure, $C\text{-RE}_2\text{O}_3$ ($\text{RE} = \text{Eu-Lu, Y}$) [7,8]. The crystal structure is bcc (space group, $Ia\bar{3}$, No. 206) with 16 molecules per unit cell. The 32 metal atoms are situated in the special positions 24(d) (C_2 point symmetry) and 8(b) (S_6 point symmetry). Both non-equivalent metal atoms are coordinated by six oxygen atoms.

2.2. Emission spectra

The emission spectra of the Eu^{3+} ion in the oxides were recorded by using the 457.9 nm blue line of a 5 W continuous wave argon ion laser, except in the case of $\text{In}_2\text{O}_3:\text{Eu}^{3+}$ in which a much better response was obtained under UV excitation (Osram HBO 150 W mercury lamp centered at 300 nm). The spectra were recorded at 77 K by using standard techniques.

Fig. 1 shows the emission spectra in the region of the ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions. At 77 K some of the weak lines observed are due to components of the ${}^5D_1 \rightarrow {}^7F_3$ transition, as demonstrated by the emission spectrum of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ under dye laser excitation at 580.6 nm (5D_0 level). This is shown in Fig. 2. The lines indicated by the arrows, in Fig. 1, are assigned to the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions occupying the S_6 site symmetry [9].

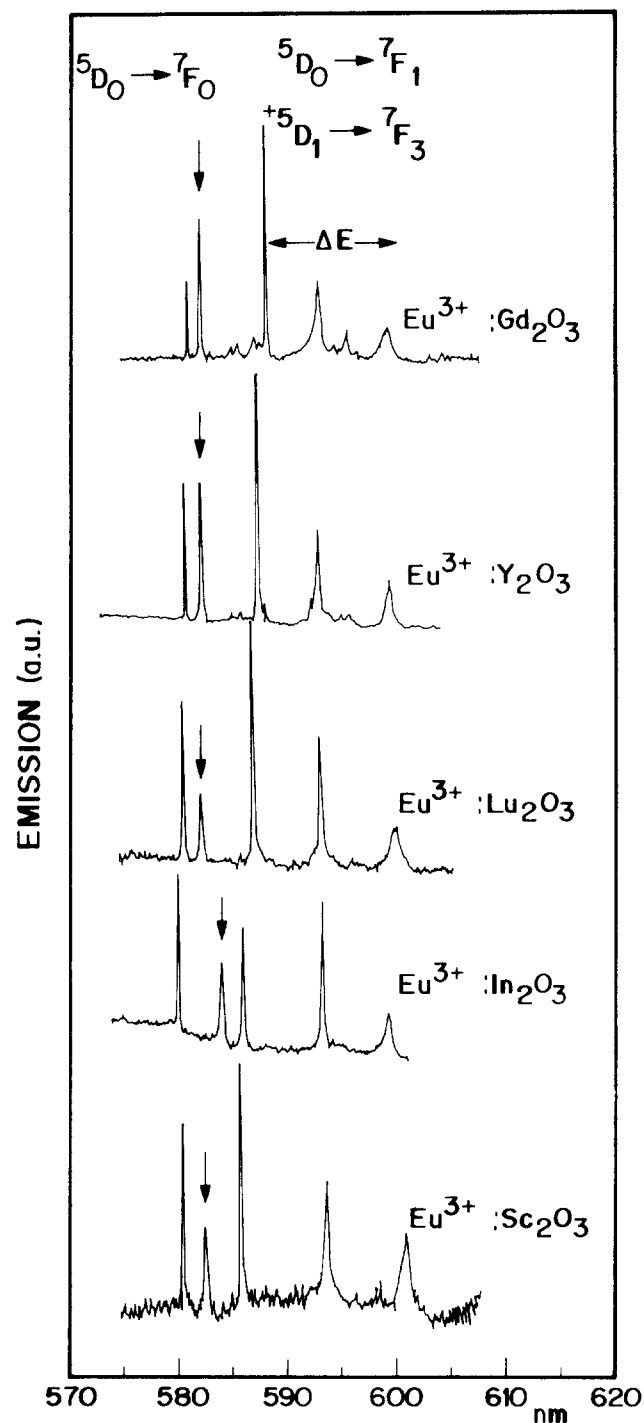


Fig. 1. Emission spectra, at 77 K , of $M_2O_3:\text{Eu}^{3+}$ in the spectral region of the ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions of the Eu^{3+} ion. The excitation wavelength is 457.9 nm except for $\text{In}_2\text{O}_3:\text{Eu}^{3+}$ (see text).

3. Theoretical aspects

According to the theory developed in Ref. [2], the relation between the maximum splitting, ΔE , of a given J level and the crystal field strength parameter N_V is given by

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

In this equation g is the degeneracy of the J level and $g_a = g$ if J is an integer and $g_a = g/2$ if J is half-integer. The cubic root, in Eq. (1), represents a geometrical average of the product over k ($= 2, 4, 6$) of the nonvanishing reduced matrix elements of the irreducible spherical tensor operators $\sum_i C^{(k)}(i)$. The index i runs over the $4f$ electrons. The crystal field strength parameter is given by

$$N_V = \left[\sum_{k,q} \left(\frac{4\pi}{2k+1} \right) |B_q^k|^2 \right]^{1/2} \quad (2)$$

where the quantities B_q^k are the so-called crystal field

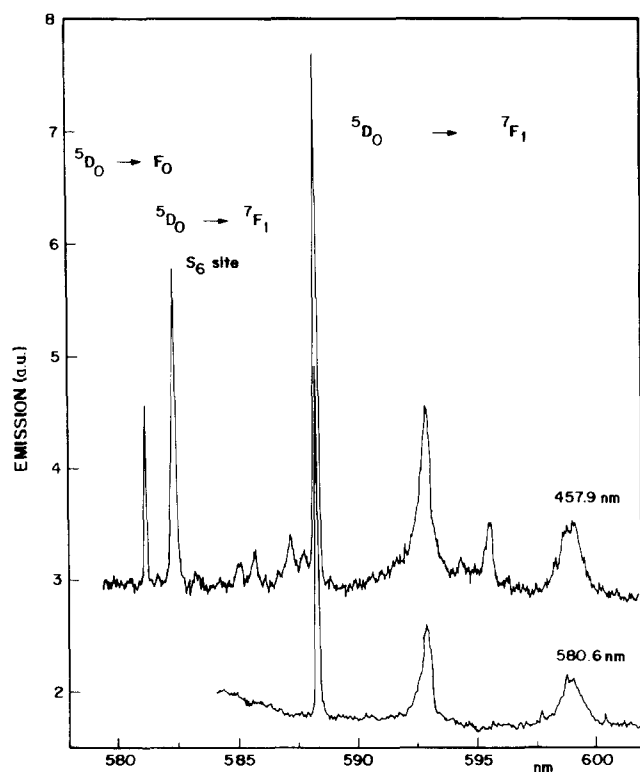


Fig. 2. Emission spectra, at 77 K, of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ in the spectral region of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions of the Eu^{3+} ion under excitation at 457.9 nm and 580.6 nm.

parameters that appear in the expression of the crystal field Hamiltonian,

$$V = \sum_{k,q,i} B_q^k C_q^{(k)}(i). \quad (3)$$

It is important to call attention to the fact that the sum over k in Eq. (2) should indeed be restricted to those values of k for which the reduced matrix elements appearing in Eq. (1) are nonvanishing. This condition can be readily noticed in the development of Eq. (1) before introducing the geometrical average over the product of reduced matrix elements [2].

Eq. (1) has proven to be quite successful in reproducing the maximum splitting of J levels of Nd^{3+} , Sm^{3+} , Dy^{3+} and Er^{3+} [2]. As already mentioned in the introduction, the obtention of this equation postulates the existence of a large number of levels belonging to a J manifold and that their repartition is approximately homogeneous. To examine the case of small J values all we have to do is to retake Eqs. (2), (4) and (10) of Ref. [2]. These are

$$(\Delta\varepsilon)^2 = \frac{1}{g} \text{tr}(P_0 V P_0 V) \quad (4a)$$

$$(\Delta\varepsilon)^2 = \frac{1}{g_a} \left(\frac{\Delta E}{2} \right)^2 (1 + \alpha_2^2 + \dots + \alpha_{g_a-2}^2 + 1) \quad (4b)$$

and

$$\text{tr}(P_0 V P_0 V) = \sum_{k,q} \frac{|B_q^k|^2}{2k+1} |\langle J \| C_{(i)}^{(k)} \| J \rangle|^2 \quad (4c)$$

$\Delta\varepsilon$ is the root-mean-square deviation of the g -fold degenerate J level under the action of the crystal field V , and P_0 is the projector operator onto the subspace defined by J . The quantities α_j ($0 < \alpha_j < 1$) are fractions which give the splittings of the levels, inside the interval ΔE , in units of $\Delta E/2$. For small J values it is necessary to take only $k=2$ in Eq. (4c). Thus, combining Eqs. (4a)–(4c) we get

$$\Delta E = \left[\frac{g_a}{g} \frac{|\langle J \| \sum_i C^{(2)}(i) \| J \rangle|^2}{\pi(2 + \alpha_2^2 + \dots + \alpha_{g_a-2}^2)} \right]^{1/2} N_V \quad (5)$$

where

$$N_V = \left[\frac{4\pi}{5} \sum_q |B_q^2|^2 \right]^{1/2}. \quad (6)$$

Let us now focus on the case $J=1$. Then only one α_j ($=\alpha$) appears in Eqs. (4b) and (5). It is not difficult to show that

$$\alpha = \frac{E_a - (E_- + \Delta E)}{\Delta E/2} \quad (7)$$

where E_a is the energy of the Stark level within the interval ΔE and E_- is the energy of the lowest Stark component of the $J(=1)$ manifold.

A rough comparison between Eqs. (1) and (5) may suggest that considerable discrepancies in their predictions may occur for small J values. We wish now to use these results in the interpretation of the experimental results presented in the previous section concerning the maximum splitting of the $^7\text{F}_1$ manifold.

4. Discussion

From the spectra shown in Fig. 1 we have measured the energies of the Stark components of the $^7\text{F}_1$ (in the C_2 site symmetry) and its maximum splitting, ΔE , for the series of oxides. The relatively large and approximately symmetric separation between the three Stark components indicates a large value of the B_2^2 crystal field parameter.

Since we are strictly interested in the $^7\text{F}_1$ manifold, we carried out a simplified phenomenological crystal field calculation taking into account only the B_0^2 and B_2^2 parameters. The starting parameters were taken from Ref. [10] and the imaginary part of B_2^2 was canceled by a proper choice of the reference axis system. The theoretical maximum splittings were calculated from Eqs. (5–7).

These results are collected in Table 1. One may note the quite good agreement between theoretical and experimental ΔE values. Since the three Stark com-

Table 1

Energy levels (Stark components) of the 7F_1 manifold, crystal field parameters of rank two and the maximum splittings ΔE of the 7F_1 in M_2O_3 ; the crystal field parameter B_{-2}^2 is equal to B_2^2 ; all values are in cm^{-1}

	Eu ³⁺ :Gd ₂ O ₃ cubic	Eu ³⁺ :Y ₂ O ₃ cubic	Eu ³⁺ :Lu ₂ O ₃ cubic	Eu ³⁺ :In ₂ O ₃ cubic	Eu ³⁺ :Sc ₂ O ₃ cubic
${}^5D_0 \rightarrow {}^7F_0$	17218	17223	17216	17233	17216
C ₂ site					
${}^5D_0 \rightarrow {}^7F_1$	17180	17176	17169	17115	17157.7
S ₆ site					
7F_1	219	201	190	176	156
	355	364	369	393	388
	535	550	563	566	591
$\Delta E(\text{experiment})$	316	349	373	390	435
Barycenter 7F_1	369.6	371.6	374.0	378.3	378.3
B_0^2	-58	-20	-6	97	68
B_2^2	-664	-743	-802	-857	-983
N_v	1491	1663	1797	1926	2158
$\Delta E(\text{theory})$	318	355	384	411	461

ponents of the 7F_1 , in our case, are approximately symmetrically separated, the influence of the fraction α , given by Eq. (7), is small. The behavior of ΔE with N_v can be better seen in the curves shown in Fig. 3.

For the sake of comparison the theoretical values of ΔE calculated from Eq. (1) are 457, 510, 552, 591 and 663 cm^{-1} , respectively, in going from gadolinium to scandium oxide.

The increase of the N_v parameter in going from gadolinium to scandium oxide is consistent with the respective decrease of the average distance metal–oxygen in the series as shown by the crystallographic data [7,8]. The rather slight increasing divergence between theoretical and experimental ΔE values, as may be noticed from Fig. 3, might be a reflection of both J -mixing effects and the fact that as the crystal

field strength increases second-order effects, like correlation effects through the crystal field Hamiltonian, can be of relevance.

These results corroborate the following points. (1) The maximum splittings of J levels in a crystal field can be satisfactorily described by an expression which is linear in the crystal field strength parameter N_v , as predicted by the theory developed in Ref. [2]. (2) In the case of small J values, in which to first order only the crystal field parameters of rank two intervene, Eqs. (5–7) above should be used instead of Eq. (1).

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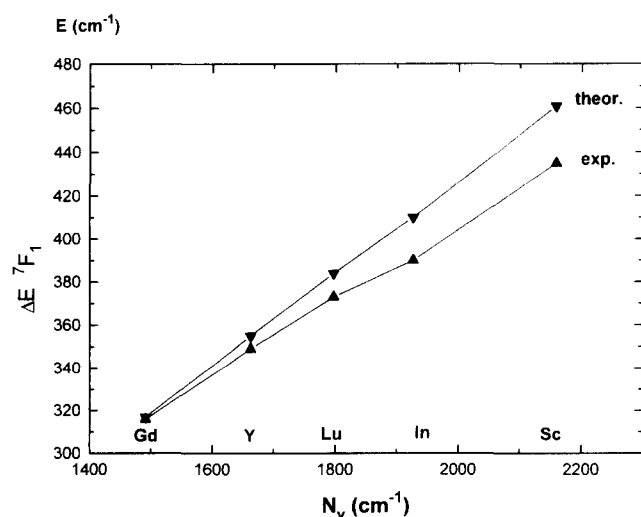


Fig. 3. Theoretical and experimental maximum splittings, ΔE , of the 7F_1 as a function of the crystal field strength parameter N_v in the series of oxides.