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Crystal field effect in RE^{3+}-doped lanthanum oxycyanamide, $La_2O_2CN_2$:RE^{3+} (RE^{3+}=Pr^{3+} and Eu^{3+})

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Abstract

The UV-vis-NIR absorption spectra of Pr^{3+} and the luminescence spectra of Pr^{3+} and Eu^{3+} in lanthanum oxycyanamide, $La_2O_2CN_2$, were measured at selected temperatures between 10 and 150, and at 77 K, respectively. The whole $4f^2$ electron configuration of Pr^{3+} was accounted for in the simulation by a phenomenological crystal field (c.f.) model including 17 refinable parameters. For Eu^{3+}, only the isolated ^7F term of the $4f^6$ configuration was considered. The simulations were initially carried out in the C_{4v} symmetry typical of the rare earth oxyhalides but the symmetry was subsequently lowered to C_{2v} with four additional real c.f. parameters (B^2_2, B^4_2, B^6_2 and B^6_6) according to the descending symmetry method. The experimental energy levels were reproduced with satisfactory r.m.s. deviations of 18 (Pr^{3+}) and 5 cm^{-1} (Eu^{3+}) and no major discrepancies between the two energy level sets were observed. The La^{3+} site symmetry cannot thus be higher than C_{2v}, but it is only slightly distorted from the C_{4v} symmetry as indicated by the low values of the four additional c.f. parameters for both RE^{3+} ions. The results for Pr^{3+} and Eu^{3+} are mutually consistent as well as with the RE oxychlorides and other RE oxycompounds. © 1998 Elsevier Science S.A.

Keywords: Lanthanum oxycyanamide; Praseodymium; Europium; Absorption; Luminescence; Energy level simulation

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1. Introduction

Lanthanum oxycyanamide, $La_2O_2CN_2$ [1], has a structure similar to that of other rare earth (RE) oxycompounds, $(REO)_nX$, consisting of alternating layers of the $(REO)_n^{n+}$ complex cations and X^{n-} anions [2]. The $(REO)_n^{n+}$ structural unit is very stable, which is assumed to be the reason for the exceptional luminescence properties of the RE oxycompounds.

The crystal structure of $La_2O_2CN_2$ has been resolved from X-ray powder diffraction data [1] by using Rietveld profile refinement method. The reported space group is tetragonal I4/mmm (No. 139), $Z=2$, with C_{4v} as the La^{3+} site symmetry. Luminescence measurements with the Eu^{3+} ion as a structural probe [3] have shown that the $(REO)_n^{n+}$ unit of the oxycyanamide is of the tetragonal type similar to those in the RE oxychlorides [4], but the La^{3+} site symmetry cannot be higher than C_{2v}. The reported crystal structure is therefore only an approximation of the real one.

In this work, the NIR-vis-UV absorption and visible luminescence of Pr^{3+} and the luminescence of Eu^{3+} in $La_2O_2CN_2$ were studied in detail. The energy level schemes deduced from the spectra were simulated by a phenomenological model accounting simultaneously for the free ion and crystal field (c.f.) interactions for Pr^{3+} but only the c.f. effect for Eu^{3+}. The results were compared to those obtained for other RE oxycompounds.

2. Experimental

2.1. Sample preparation

The polycrystalline samples of Pr^{3+}- and Eu^{3+}-doped lanthanum oxycyanamide were prepared by a reaction between the doped ($x_{Pr}=0.05$ and $x_{Eu}=0.01$) La_2O_3, gaseous ammonia and a graphite boat. The experimental conditions for this exceptional reaction were as follows: temperature, 950°C; time, 12 h; and NH_3 flow rate, 1000 cm^3 min^{-1}. The purity of the samples was verified by routine X-ray powder diffraction measurements. The ab-

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sence of any impurity lines in the optical spectra confirmed the XPD results.

2.2. Optical absorption and luminescence measurements

The optical absorption spectra of the Pr^{3+}-doped $La_2O_2CN_2$ were measured with a Cary 5E UV-vis-NIR spectrophotometer from 400 to 2500 nm at selected temperatures between 10 and 150 K using a closed circuit helium cryostat. The instrument reproducibility was 0.03 nm in the UV-vis and 0.12 in the NIR range. The sample was prepared by compressing a mixture of the oxycyanamide and KBr to a transparent disk of 1-mm thickness.

The luminescence spectra of the Pr^{3+}- and Eu^{3+}-doped lanthanum oxycyanamides were measured from 500 to 720 nm at 77 K maintained by an immersion-type liquid N_2 cryostat. The luminescence was excited by a Carl Zeiss ILA 120-1 Ar^+ ion laser at 488.0 (Pr^{3+}), 457.9 and 514.5 nm (Eu^{3+}). A Czerny-Turner type 1-m Jobin-Yvon double monochromator and a Hamamatsu R950 detector were used for the detection of luminescence. The resolution of the setup was better than 1 cm^{-1}.

2.3. Phenomenological simulation of the energy level schemes

The total Hamiltonian H describing the interactions within the $4f^N$ electron configurations is composed of two parts: one accounting for the free ion energy level structure (H_{FI}) and the other (H_{CF}) the energy level splitting caused by the crystal field [5]. The effective Hamiltonian used in this study is presented in Eq. (1).

$$H = \left[H_0 - \sum_{k=0}^{n} E_k(\mathrm{nf,nf})\, e^k + \zeta_{4f} A_{SO} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \right] + \left[\sum_{k,q,i} B^k_q C^k_q(i) \right] \qquad (1)$$

where E_k are the Racah parameters describing the electron repulsion, ζ_{4f} is the spin-orbit coupling constant, α, β and γ are the Trees parameters describing the two-body configuration interactions and B^k_q are the crystal field parameters. The other symbols are described elsewhere [5,6].

In agreement with preliminary structural data for $La_2O_2CN_2$, the spectroscopic properties showed a close similarity to those of the tetragonal RE oxychlorides, REOCl. Therefore, the $C_{4v} \rightarrow C_{2v}$ descending symmetry method was applied in the c.f. simulations, i.e. the symmetry was first considered to be C_{4v} and thereafter lowered to C_{2v} by adding more c.f. parameters. In this manner, the physical reality of the results can usually be ensured. The C_{4v} symmetry restricts the number of the c.f. parameters to five (B^2_0, B^4_0, B^4_4, B^6_0 and B^6_4) and the lowering of the symmetry to C_{2v} introduces four additional parameters (B^2_2, B^4_2, B^6_2 and B^6_6). The use of the descending symmetry method requires that the actual symmetry is close to the higher one. The additional c.f. parameters usually assume values close to zero.

The phenomenological simulation of the Pr^{3+} ion employed the whole $4f^2$ electron configuration as the untruncated basis set. The complete $4f^6$ configuration of the Eu^{3+} ion consists of 3003 Stark levels and, in order to avoid computational problems, only the 49 Stark levels of the isolated ^7F ground term were included in the simulation. This naturally excludes the simulation of the free ion interactions but can be considered justified because of the energetic isolation of the ground multiplet and the nature of the c.f. operator acting only within the ^7F multiplet.

The calculations were carried out with the computer program REEL [7] which is capable of treating simultaneously both free ion and c.f. interactions through matrix diagonalization and least-squares calculations. The standard root mean square (r.m.s.) deviation σ between the experimental and calculated energy level values was used to evaluate the quality of the simulations.

3. Results and discussion

From the interpretation of the optical absorption and luminescence spectra of $La_2O_2CN_2$:Pr^{3+} (Fig. 1) 31 of the total of 91 energy levels were obtained. The $^3H_5$ and $^1S_0$ levels could not be observed because they were out of the wavelength range of the experimental setup. Of the other energy levels only $^1G_4$ and $^3P_2$ were totally unobserved. In the luminescence spectrum of the Eu^{3+}-doped sample (Fig. 2), 17 of the possible 49 Stark components of the $^7F_{0-6}$ levels were observed: nearly a complete set of the $^7F_{0-3}$ levels, some $^7F_4$ but no $^7F_{5-6}$ levels which lack in most cases.

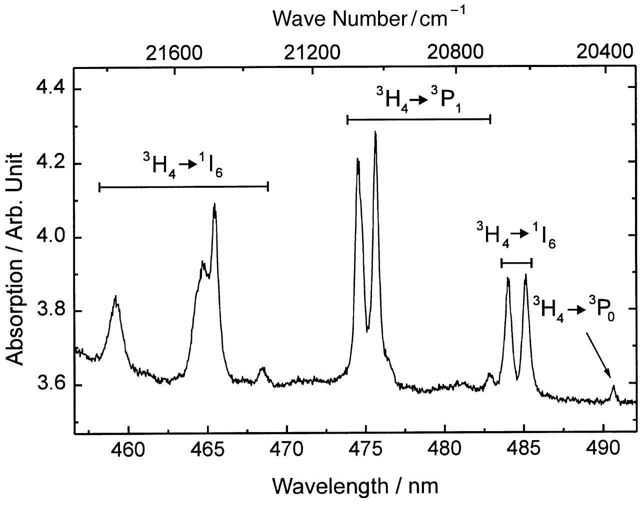

Fig. 1. A part of the absorption spectrum of $La_2O_2CN_2$:Pr^{3+} at 10 K.

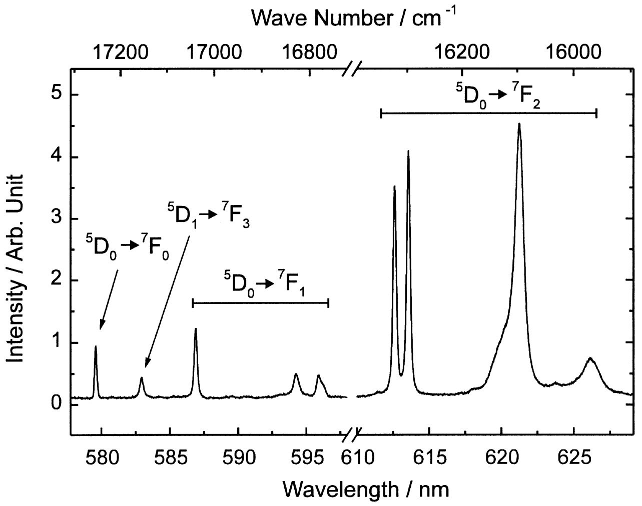

Fig. 2. A part of the luminescence spectrum of $La_2O_2CN_2:Eu^{3+}$ at 77 K ($\lambda_{exc}=457.9$ nm).

Because of the apparent similarities between the spectra of the oxycyanamides and $LaOCl:Eu^{3+}$ [4], as well as PrOCl [8], the energy level simulations were initially carried out in the C_{4v} symmetry of the oxychlorides. The free ion and c.f. parameter values for $LaOCl:Eu^{3+}$ and PrOCl were used as the starting values. All the parameter values were refined freely, except for the Trees parameter γ, whose value was fixed to a customary 1422 cm^{-1}, because its value is greatly influenced by the position of the unobserved $^1S_0$ level [8]. According to the descending symmetry method, the calculations carried out in the lower C_{2v} symmetry yielded a satisfactory agreement between the experimental and calculated values with r.m.s. deviations of 18 (Pr^{3+}) and 5 cm^{-1} (Eu^{3+}). The correctness of the simulations was revealed by the absence of any large discrepancies between the observed and calculated energy level schemes (Fig. 3).

The B_0^2 parameter values obtained were very similar to those of the oxychlorides (Table 1). The fourth (B_q^4) and sixth rank (B_q^6) parameters represent the mid- and long-range c.f. interactions (mainly between the X^{n-} anion layer and the RE^{3+} ion). These parameter values differed significantly from the oxychloride ones, but were very similar to those of lanthanum oxymolybdate (Table 2). The fourth and sixth rank parameters were also the least well-defined ones, as is seen from their estimated standard deviations (Table 1). This probably results from the sparsity of both observed energy level schemes (only about a third of the total).

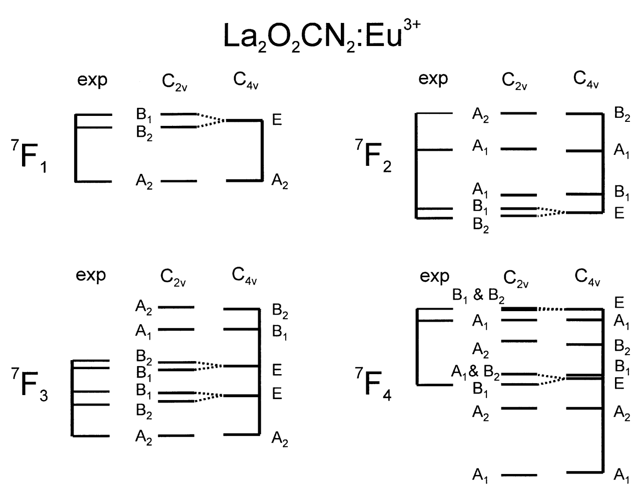

Fig. 3. A comparison the experimental and calculated $^7F_{1-4}$ energy level schemes of $La_2O_2CN_2:Eu^{3+}$ in the C_{4v} and C_{2v} symmetries.

In the case of the Eu^{3+}-doped sample, the values of the c.f. parameters not allowed in C_{4v} were small (Table 1), similar to those obtained for lanthanum oxymolybdate, $La_2O_2MoO_4$ [9], oxynitrate, $LaONO_3$ [10], and oxysulfate, $La_2O_2SO_4$ [11] (Table 2). Despite the low values for these additional parameters, the RE^{3+} site symmetry is C_2 [12] and C_1 [13] in oxymolybdate and oxysulfate, respectively. Together with the oxynitrates, whose structure has not either been solved in a satisfactory manner, although a tetragonal structure with the C_{4v} symmetry has been suggested [14], the actual RE^{3+} site symmetry in the oxycyanamide could be even lower than C_{2v}.

No c.f. analyses of the Pr^{3+} energy level scheme have been reported in the C_{2v} symmetry for the RE oxy-compounds, and thus there are no c.f. parameter values to be compared with the current results. Since the unit cell volumes of the two doped oxycyanamides are practically the same, the c.f. parameter values should be closer to each other than between $LaOCl:Eu^{3+}$ and PrOCl. This was, indeed, what was observed (Table 1). However, the absolute values of the B_0^4 and B_2^6 parameters differ significantly. This is also reflected in the relative c.f. strength parameters S^k (Table 1) [15], whose values indicate that the mid- and long-range c.f. interactions are clearly stronger in the Eu^{3+}-doped sample. The overall c.f. strength parameters S [16,17] of the oxycyanamides behave very similarly to the oxychloride ones, but the difference is expectedly smaller (Table 1). All in all, the results of the two simulations are consistent, even if there always is a possibility that the global minima were not obtained, which may occur rather frequently for symmetries as low as C_{2v} and when a large number of energy level values are unknown.

4. Conclusions

The energy levels schemes of Pr^{3+} and Eu^{3+} in the lanthanum oxycyanamide matrix were successfully simulated in the C_{2v} symmetry by a phenomenological c.f. model. The calculations resulted in satisfactory r.m.s. deviation values of 18 (Pr^{3+}) and 5 cm^{-1} (Eu^{3+}) and no major discrepancies between the observed and calculated energy level schemes were observed. C_{2v} is thus the

Table 1
The free-ion, crystal field and crystal field strength parameters S (in cm^{-1}) for $La_2O_2CN_2$:RE^{3+} ($RE^{3+} = Pr^{3+}$ and Eu^{3+}) in the C_{4v} and C_{2v} symmetries as well as for PrOCl [8] and LaOCl:Eu^{3+} [4]

Parameter	$La_2O_2CN_2$:Pr^{3+}		PrOCl	$La_2O_2CN_2$:Eu^{3+}		LaOCl:Eu^{3+}
	C_{4v}	C_{2v}	C_{4v}	C_{4v}	C_{2v}	C_{4v}
E_0	9642(2)	9646(2)	5368(2)			
E_1	4576(2)	4477(2)	4496(2)			
E_2	21.00(2)	20.93(2)	21.74(2)			
E_3	454.4(2)	454.3(2)	456.8(1)			
α	18.3(1)	18.2(1)	23.6(1)			
β	−647(9)	−630(9)	−676(2)			
γ	[1422]	[1422]	[1422]			
ζ	746(1)	745(1)	742(1)			
B^2_0	−1074(9)	−1067(9)	−842(9)	−1053(21)	−1059(23)	−1281(9)
B^2_2		±118(11)			±99(14)	
B^4_0	−967(22)	−927(23)	−550(24)	−1366(24)	−1375(27)	−467(20)
B^4_2		±57(35)			±1(33)	
B^4_4	±700(22)	692(24)	±826(16)	±660(27)	663(29)	±1036(12)
B^6_0	−709(45)	−560(49)	1092(37)	−502(94)	−429(99)	582(28)
B^6_2		∓397(73)			∓129(45)	
B^6_4	±109(52)	214(62)	±27(27)	±901(27)	920(39)	±334(17)
B^6_6		±79(54)			±14(26)	
S^2	1074	1080	842	1053	1068	1281
S^4	1384	1350	1291	1654	1664	1538
S^6	726	856	1092	1370	1382	750
S	402	405	374	472	477	460
σ	17	18	17	4	5	7

The numbers in parentheses refer to the estimated standard deviations of the parameters. The values in square brackets were not refined.

highest possible La^{3+} site symmetry rendering the reported crystal structure of $La_2O_2CN_2$ only an approximation. The simulations for the two ions resulted in low values for the c.f. parameters B^2_2, B^4_2, B^6_2 and B^6_6 indicating only a small distortion from the C_{4v} symmetry. In order to solve the structural puzzle, the crystal structure of $La_2O_2CN_2$ is currently being investigated by combining X-ray, neutron and electron diffraction methods.

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Table 2
The crystal field parameter values (in cm^{-1}) for $La_2O_2CN_2$:Eu^{3+}, $La_2O_2MoO_4$:Eu^{3+} [9], $LaONO_3$:Eu^{3+} [10] and $La_2O_2SO_4$:Eu^{3+} [11] in the C_{2v} symmetry

Parameter	$La_2O_2CN_2$	$La_2O_2MoO_4$	$LaONO_3$	$La_2O_2SO_4$
B^2_0	−1059(21)	−995(18)	−1149(21)	−981(9)
B^2_2	99(14)	133(12)	−133(13)	117(7)
B^4_0	−1375(24)	−1394(22)	−1005(26)	−651(12)
B^4_2	1(33)	131(30)	224(35)	258(10)
B^4_4	663(29)	675(22)	863(19)	−720(10)
B^6_0	−429(99)	−600(68)	168(44)	556(20)
B^6_2	−129(45)	19(37)	139(34)	−120(22)
B^6_4	920(39)	696(29)	165(25)	−278(9)
B^6_6	14(26)	36(19)	−168(27)	25(13)
σ	5	7	7	8

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