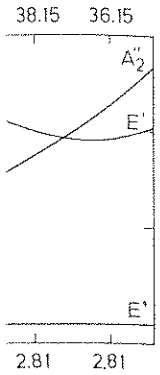

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CRYSTAL FIELD ANALYSIS FOR EMISSION SPECTRA OF LaOCl:Eu^{3+} UNDER HIGH PRESSURE

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The effects of pressure on the emission spectra of Eu^{3+} activated LaOCl:Eu^{3+} were measured at room temperature up to 136 kbar. At various pressures between 0 and 136 kbar, the crystal field parameters have been determined via the intermediate coupling wavefunction and *J*-mixing, which reproduced the experimental ^7F_J Stark energy level scheme within a mean square deviation of a few cm^{-1}. The pressure dependence of the spin–orbit interaction and intensity ratio are also discussed.

1. Introduction

For many years, the $4f^6$ configuration spectra of Eu^{3+} ions have been used as an experimental backing for crystal field (c.f.) theories due to the large energy gap between the ground ^7F_J septet and the rest of the configuration, and the fact that the c.f. operator only allows mixing between levels of the same multiplicity. Recently, Hölsä and Porcher [1, 2] have calculated the c.f. parameters for the whole REOX:Eu^{3+} series (RE = Y, La, Gd; X = Cl, Br, I), which simulate well the splittings of the ^7F_J levels. However, no high pressure fluorescence studies have been made to determine the effect of pressure on the c.f. parameters. In this study, we attempt to calculate the c.f. parameters of the Eu^{3+} doped in LaOCl under high pressure from the emission spectra up to 136 kbar.

2. Experimental

Polycrystalline powders of LaOCl:Eu^{3+} doped with 5 mol% europium replacing the lanthanum were prepared by a solid state reaction with La_2O_3, Eu_2O_3 and NH_4Cl. All products were routinely analyzed by X-ray powder diffraction. The LaOCl:Eu^{3+} has a tetragonal layer structure, in which the RE^{3+} ion is coordinated to four oxygen and five chlorine atoms with C_{4v} point site symmetry.

The emission spectra were recorded on a GDM-1000 grating double monochromator combined with a cooled RCA C31034 photomultiplier and 5Cl photo counting system. The fluorescence was excited by 4880 Å the line of an Ar ion laser. The pressure was generated by a diamond anvil cell. Methanol–ethanol was used as the hydrostatic pressure transmitting medium. Pressure was determined by the ruby fluorescence scale.

In the emission spectra of LaOCl:Eu^{3+} more than 20 lines were observed at room temperature and various pressures up to 136 kbar. These lines can be attributed to the $^5D_0 \rightarrow {}^7F_{0-4}$ and $^5D_1 \rightarrow {}^7F_{2-4}$ transitions [1]. The energy of the lines observed at ambient pressure and their red shift rates with pressure are summarized in table I. The corresponding energy levels and their pressure coefficients are listed in table II, where the energies are given in cm^{-1} with respect to the ground state $^7F_0$ and the unit of pressure is kbar. In addition, with increasing pressure the intensity ratio, $^5D_0 \rightarrow {}^7F_0/{}^5D_0 \rightarrow {}^7F_2$, obviously decreases.

3. Crystal field calculation

By using an intermediate coupling wavefunction and *J*-mixing [3], the c.f. simulations were carried out on the basis of the strongly reduced 49 ^7F_J stark levels of Eu^{3+} under pressure. For the

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Table I.
The energy of lines observed in the emission spectra of LaOCl:Eu^{3+} at ambient pressure and their red shift rate with increasing pressure

Transition	Assignment	Energy (cm^{-1})	Shift rate (cm^{-1}/kbar)
$^5D_0 \rightarrow {}^7F_5$	$A_1 \rightarrow E$	13073	
	$A_1 \rightarrow A_1$	13281	
	$A_1 \rightarrow E$	13364	
	$A_1 \rightarrow E$	13540	
$^5D_0 \rightarrow {}^7F_4$	$A_1 \rightarrow E$	14256	0.37
	$A_1 \rightarrow A_1$	14287	0.48
	$A_1 \rightarrow E$	14353	0.10
	$A_1 \rightarrow A_1$	14551	0.28
$^5D_0 \rightarrow {}^7F_3$	$A_1 \rightarrow E$	15261	0.32
	$A_1 \rightarrow E$	15374	0.57
$^5D_1 \rightarrow {}^7F_4$	$A_2 \rightarrow E$	15959	0.26
	$A_2 \rightarrow A_2$	16107	0.61
$^5D_0 \rightarrow {}^7F_2$	$A_1 \rightarrow A_1$	16173	0.64
	$A_1 \rightarrow E$	16248	0.43
$^5D_0 \rightarrow {}^7F_1$	$A_1 \rightarrow E$	16798	0.56
	$A_1 \rightarrow A_2$	17090	1.07
$^5D_1 \rightarrow {}^7F_3$	$A_2 \rightarrow E$	16978	0.32
	$E \rightarrow B''$	17046	0.60
	$E \rightarrow E$	17158	0.67
	$E \rightarrow A_2$	17167	0.65
$^5D_0 \rightarrow {}^7F_0$	$A_1 \rightarrow A_1$	17279	0.74
$^5D_1 \rightarrow {}^7F_2$	$A_2 \rightarrow E$	17958	0.30
	$E \rightarrow E$	18030	0.43
	$E \rightarrow B''$	18059	0.56

C_{4v} symmetry occupied by the Eu^{3+} ion in LaOCl the c.f. Hamiltonian is written as a polynomial:

$$H_{\text{c.f.}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 (C_{-4}^4 + C_4^4) + B_0^6 C_0^6 + B_4^6 (C_{-4}^6 + C_4^6) ,$$

where the tensorial operators C_q^k are related to the spherical harmonics Y_q^k by the equation

$$C_q^k = [4\pi/(2k+1)]^{1/2} Y_q^k .$$

To derive the five B_q^k c.f. parameters there are 28 and 21 energy levels measured by ourselves at ambient pressure and high pressure respectively (see table II). To make the experimental and calculated bary centers coincide, 6 intermediate parameters have to be introduced, one for each ^7F_J level. The experimental energy levels are fitted by least square calculation (l.s.c.) to give

Table II
Observed energy levels at ambient pressure and their pressure coefficient for LaOCl:Eu^{3+}

		Energy (cm^{-1})	Pressure coefficient (cm^{-1}/kbar)
$^7F_0$	A_1	0	
$^7F_1$	A_2	189	0.27
	E	482	−0.20
$^7F_2$	B″	1003	−0.23
	E	1030	−0.30
	A_1	1105	−0.09
$^7F_3$	A_2	1894	−0.13
	E	1906	−0.18
	E	2015	−0.39
	B″	2016	−0.19
$^7F_4$	A_1	2728	−0.47
	A_2	2881	−0.04
	E	2926	−0.60
	A_1	2991	−0.26
	E	3024	−0.38
$^7F_5$	E	3738	
	E	3914	
	A_1	3997	
	E	4205	
$^5D_0$	A_1	17279	−0.74
$^5D_1$	A_2	18989	−0.66
	E	19062	−0.79

the 5 B_q^k parameters. As starting values for the l.s.c. we used the B_q^k values obtained by Hölsä and Porcher [1]. The sets of the c.f. parameters at various pressures obtained from the refining calculations are presented in table III. It can be seen that the small rms deviations, no larger than 5 cm^{-1}, indicate a quite good simulation between the experimental and calculated energy levels.

Table III
Crystal field parameters and rms deviations σ (in cm^{-1}) for LaOCl:Eu^{3+} at various pressures (in kbar)

Pressure	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	σ
0	−1347	−476	1051	913	282	5
20	−1302	−479	1051	958	287	5
40	−1257	−484	1047	972	292	4
60	−1196	−494	1065	959	271	3
80	−1155	−500	1056	955	281	4
100	−1119	−565	1001	973	297	3
120	−1070	−553	962	956	386	3
136	−1053	−611	955	1009	321	4

4. Discussion

In this section, we will concentrate on the discussion of two aspects: (A) the pressure dependence of the spin–orbit interaction, and (B) the pressure dependence of the intensity ratio.

4.1. Spin–orbit interaction

Using the observed and calculated energy levels, the center of gravity (cg) of each ^7F_J ($J = 0$–4) manifold can easily be obtained, namely,

$$E_{cg}(^7F_1) = 385 - 0.05p \quad (1a)$$

$$E_{cg}(^7F_2) = 1111 - 0.25p \quad (1b)$$

$$E_{cg}(^7F_3) = 1977 - 0.31p \quad (1c)$$

$$E_{cg}(^7F_4) = 2962 - 0.40p\ . \quad (1d)$$

The spin–orbit coupling parameter, $\lambda_{4f}(J, p)$, then can be determined from E_{cg} by the use of the well-known Landé rule:

$$E_{cg}(^7F_J) - E_{cg}(^7F_{J-1}) = J\lambda_{4f}(J, p)\ ,$$

where

$$\lambda_{4f}(1, p) = 385 - 0.05p$$

$$\lambda_{4f}(2, p) = 363 - 0.10p$$

$$\lambda_{4f}(3, p) = 289 - 0.02p$$

$$\lambda_{4f}(4, p) = 246 - 0.02p\ .$$

These results indicate that the spin–orbit coupling parameter is a function of both the quantum number J and pressure p, and with increasing pressure all the cg and λ_{4f} decrease almost linearly.

In a first approximation the spin–orbit coupling parameter of each ^7F_J manifold should be independent of the quantum number J. Therefore, we can get the average spin–orbit coupling parameter $\lambda_{4f}(p)$ of the ^7F multiplet,

$$\lambda_{4f}(p) = 321 - 0.05p\ ,$$

and, furthermore, we can estimate the compressibility of the orbital radius r_{4f} for the 4f electrons in the active ion Eu^{3+}:

$$\frac{d\ln\langle r_{4f}\rangle}{dp} = -\frac{1}{3}\frac{d\ln\lambda_{4f}(p)}{dp} = 0.05\ (\text{Mbar})^{-1}$$

in which $\langle r_{4f}\rangle$ stands for the radial integral. This value is comparable with the value 0.08 Mbar^{-1}, which was obtained by Huber et al. [4] on the Eu^{3+} ion in EuP_5O_{14}.

4.2. Intensity ratio

From the point of view of the pseudo-multipolar field, via the J-mixing effect [5], the intensity ratio $R(^5D_0 \rightarrow {}^7F_0/{}^5D_0 \rightarrow {}^7F_2)$ is related to the crystal field parameters B_q^k, namely,

$$R = 0.5|\sin\tfrac{1}{2}\beta|^2 \quad (2)$$

where

$$\beta = \tan^{-1}\left(\frac{0.45B_0^2}{E_{cg}(^7F_2) + 0.105B_0^2 - 0.1B_0^4}\right). \quad (3)$$

From table III, the pressure dependence of B_0^2 and B_0^4 can be described by

$$B_0^2 = -1350 + 2.32p$$

$$B_0^4 = -474 - 0.32p\ . \quad (4)$$

Eqs. (1b) and (4) are substituted into eq. (3), we then have

$$\beta = \tan^{-1}\left(\frac{-607.5 + 1.044p}{1016.65 + 0.0256p}\right). \quad (5)$$

From eq. (5), it can be seen that the angle β will reduce with pressure, resulting in a decrease of the intensity ratio R. This is qualitatively in accord with our experimental result.

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