

Absorption and laser excited fluorescence of $\text{Ho}^{3+} : \text{LaF}_3$

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Abstract. The absorption and fluorescence spectra of $\text{Ho}^{3+} : \text{LaF}_3$, in the wavelength region from 4000 Å to 7500 Å have been reinvestigated incorporating polarization features, for the first time. The fluorescence spectrum, recorded using a spectrophotometer assembled in the laboratory, was excited with a He-Ne laser and an Ar^+ laser. The present study enabled the interpretation of the data in terms of the C_{2v} site symmetry of Ho^{3+} and most of the Stark components of the observed states have been classified under the irreducible representations of the C_{2v} point group.

Keywords. $\text{Ho}^{3+} : \text{LaF}_3$; polarized absorption and fluorescence; symmetry classification.

1. Introduction

The SLJ states of the lowest configuration of Ho^{3+} , $4f^{10}$, have been fairly well established by various studies made from holmium salts and Ho^{3+} as impurity in various matrices. The holmium salts studied so far are: $\text{Ho}_2(\text{SO}_4)_3$ (Gobrecht 1938; Mehan and Nutting 1939), HoCl_3 , Ho_2O_3 (Khale 1956; Singh 1957) $\text{Ho}_2(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Spedding and Rothwell 1968) and HoFeO_3 (Walling and White 1974). Dieke and Pandey (1964) studied the absorption and fluorescence spectra of $\text{Ho}^{3+} : \text{LaCl}_3$ in detail, while Rajnak and Krupke (1968) gave a comprehensive theoretical interpretation of $\text{Ho}^{3+} : \text{LaCl}_3$ spectra. The other crystals containing Ho^{3+} that are studied so far are: CaF_2 (Merz and Parshan 1967), YGaG , YIG (Johnson *et al* 1969), CaWO_4 (Wortman and Sanders 1970), YPO_4 (Becker 1971), YAIO_3 (Weber and Matsinger 1972) LiTmF_4 (Wortman *et al* 1973) and very recently in tellurite, calibo and phosphate glasses (Reisfeld and Hormadaly 1976). Caspers *et al* (1970) have extensively studied $\text{Ho}^{3+} : \text{LaF}_3$ both in absorption as well as in fluorescence at 1.5°K and have established the complete energy level scheme up to 26,000 cm^{-1} . They also calculated the intermediate coupling free ion energy levels with an rms deviation of about 29 cm^{-1} . However, there is no study so far on the polarization features of the $\text{Ho}^{3+} : \text{LaF}_3$ spectra or on the site symmetry of Ho^{3+} in LaF_3 .

In the present work the absorption and fluorescence spectra of $\text{Ho}^{3+} : \text{LaF}_3$ have been reinvestigated incorporating the polarization features. The polarized absorption spectrum in the region 4000–7000 Å, photographed at 80°K and the laser excited polarized fluorescence spectra also recorded at 80° K, are reported for the first time in this work. The polarization features of the observed spectra have been interpreted in terms of C_{2v} site symmetry of Ho^{3+} and most of the Stark components of the states, observed in absorption and fluorescence have been classified according to the irreducible representations of this symmetry group.

2. Ho³⁺ site symmetry and selection rules

The crystal structure of LaF₃ has not been established uniquely. Different experimental studies have indicated different crystal structures for this crystal. For example, the EPR measurements made on a number of rare-earth ions doped in LaF₃ (Baker and Rubins 1969) are consistent with a hexagonal and hexamolecular unit cell belonging to C_{6v}³ space group. These results are further substantiated by neutron scattering studies (Collete and Zelwer 1966). However, two more symmetric structures viz. D_{6h}³ and D_{3d}⁴ have been proposed on the basis of x-ray measurements (Mansman 1964). The Raman spectra (Bauman and Porto 1967) of LaF₃ could be interpreted assuming D_{3d}⁴ structure but only small deviations from D_{6h}³ structure were observed. The polarization features of the optical spectra of Pr³⁺:LaF₃ (Wong *et al* 1963) and Eu³⁺:LaF₃ (Kumar *et al* 1977) could be explained on the basis of D_{6h}³ structure, indicating that D_{6h}³ structure is not far from reality. The present study is also compatible with D_{6h}³ structure.

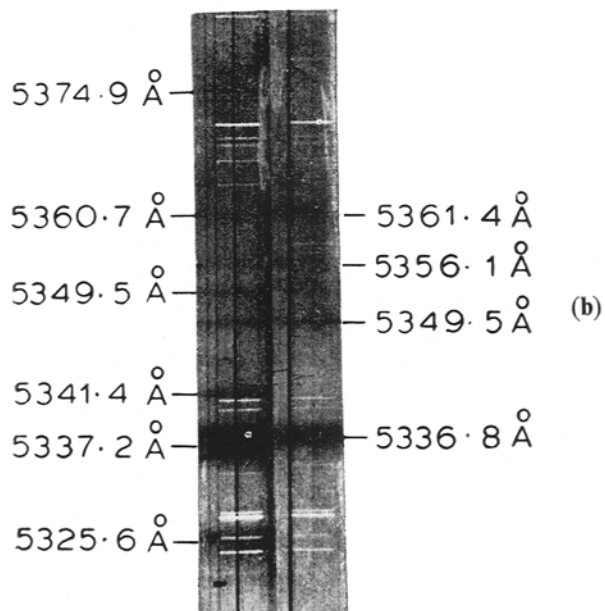
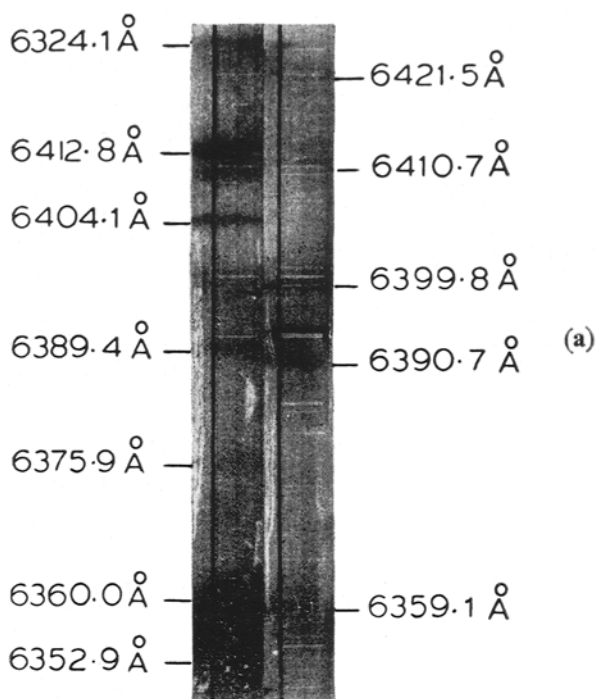
The site symmetry of La ions is C_{2v} in D_{6h}³ space symmetry of LaF₃ and the unit cell is hexamolecular. The six La ions lie on two planes (La planes) forming equilateral triangles which are rotated by 60° with respect to each other with a separation of *c*/2 between the planes. The crystal *z*-axis or *c*-axis is perpendicular to ionic *c*-axis. To derive the selection rules a co-ordinate system XYZ in which X and Z lie in a plane perpendicular to *c*-axis (*Y*-axis coinciding with *c*-axis) is used. The horizontal plane being a symmetry plane the *X*-axis and the *Z*-axis are indistinguishable. This degeneracy of *X* and *Z*-axes leads to ambiguity in the classification of various states in terms of C_{2v} irreducible representations. Specifically, it is not always possible to distinguish between A₁ and B₁ or between A₂ and B₂ (A₁, A₂, B₁ and B₂ are the irreducible representations of C_{2v} point group).

The selection rules for electric dipole transitions are given in table 1. The σ-transition refer to the electric vector perpendicular to *c*-axis (*Y*-axis) of the crystal and the π-transition refer to the electric vector parallel to the *c*-axis.

3. Experimental details

A single crystal of LaF₃ containing Ho³⁺ as impurity purchased from the Optovac Co. (USA), was kindly loaned to us by Professor H P Broida of the University of California at Santa Barbara. The crystal (10 mm × 7 mm × 4 mm) is of very good optical quality and according to the manufacturer's specifications, the holmium concentration in the crystal is 0.5% and the *c*-axis is parallel to 4 mm side. This *c*-axis has been further checked by viewing the crystal under a polarization microscope. From the present fluorescence data, it is found that the LaF₃ crystal contains an unknown but small quantity (<0.1 per cent) of praseodymium also.

The absorption spectrum in the region 4000–7000 Å at 80° K has been photographed on a 3.4 m Jarrell-Ash plane grating (30,000 LPI) spectrograph at a dispersion of 2.5 Å/mm. A 750 watt tungsten (projector) lamp provided the continuum. The plates were measured on a Carl-Zeiss Model B Abbe comparator.



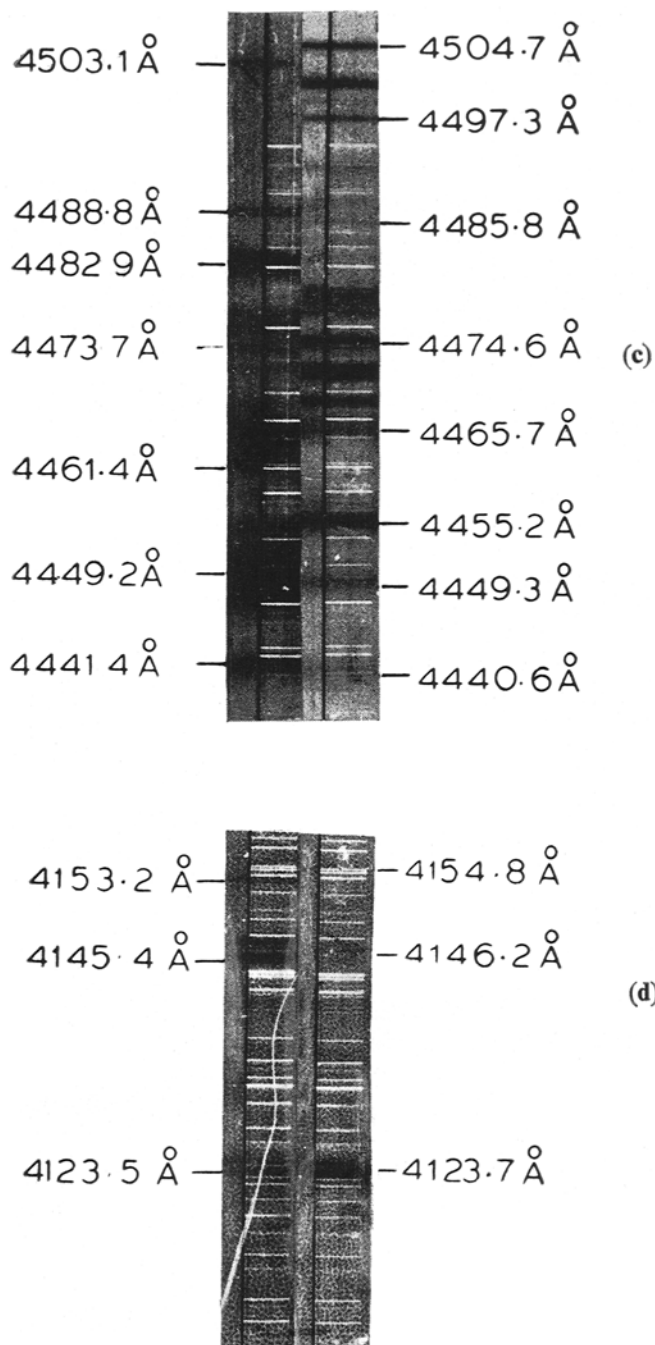


Figure 1. Ho^{3+} in LaF_3 : Polarized absorption at 80°K , (a) 6400 Å group (b) 5305 Å group (c) 4480 Å (d) 4135 Å

A He-Ne laser and an Ar⁺ laser (Spectra Physics USA, Model No. 165-03) were used to excite the fluorescence. The He-Ne laser has been fabricated in the laboratory. It consists of a 2m long plasma tube (4 mm dia) terminated at Brewster's windows. A dielectric coated spherical mirror (radius of curvature 2 m) and a dielectric coated half prism at Brewster's angle, form the laser cavity. A 5 kV, 100 mA unregulated power supply is used for exciting the plasma tube.

The He-Ne laser excited fluorescence spectrum has been photographed on a 3-prism glass spectrograph (Carl-Zeiss) fitted with 27 cm camera. The Ar⁺ laser excited fluorescence has been recorded using a spectrophotometer assembled in the laboratory (Rao *et al* 1976). The dispersion on the recorder chart paper of the spectrophotometer is variable between 5 Å/mm to 1.0 Å/mm and the wavelengths measured, are accurate to ± 1.5 Å. A demountable cold finger liquid nitrogen dewar was used for low temperature work. The minimum temperature to which the crystal mounted in the dewar, could be cooled is about 80° K. A Glan-Thomson polarizer was used to study the polarization features of the absorption and fluorescence spectra.

4. Absorption spectrum

The absorption spectrum photographed at 80° K in the range 4000–7000 Å consists of four groups of lines around 4135 Å, 4480 Å, 5305 Å and 6400 Å (figure 1). All the absorption lines are completely polarized. By comparison with the absorption data reported by Caspers *et al* (1970) all the lines in 4135 Å and 5305 Å groups are easily identified as due to electric dipole transitions ${}^5I_8(Z) - {}^5G_5(J)$ and ${}^5I_8(Z) - {}^5F_4(E)$, ${}^5S_2(E^\circ)$, respectively. When such comparison is made for 6400 Å group, it is found that though most of the lines of this group are also due to electric dipole transitions ${}^5I_8(Z) - {}^5F_5(D)$, six additional lines observed on the higher energy side of the main absorption lines could not be assigned. These additional lines are tentatively assigned to be from vibronic transitions. Most of the lines of the remaining absorption group around 4480 Å are identified as due to electric dipole transition ${}^5I_8(Z) - {}^5G_6(I)$. However, it is not possible to assign any transitions to some ten lines observed on the low energy side of the ${}^5I_8(Z) - {}^5G_6(I)$ absorption group.

5. Fluorescence spectrum

The fluorescence spectrum has been recorded at 80° K in the wavelength region 4500–7600 Å, using 6328 Å laser line of the He-Ne laser and various laser lines of the Ar⁺ laser as excitations. The fluorescence excited by 6328 Å laser line is identified to correspond to the electric dipole transition ${}^5F_5(D) - {}^5I_8(Z)$ while the states ${}^5F_3(F)$, ${}^5F_4(E)$, ${}^5S_2(E^\circ)$ and ${}^5F_5(D)$ are found to fluoresce when excited by Ar⁺ laser. The various transitions (figure 2) involved in fluorescence are:

$$({}^5F_3, {}^5F_4, {}^5S_2, {}^5F_5) \text{ — } {}^5I_8 \text{ and}$$

$$({}^5F_3, {}^5F_4, {}^5S_2) \text{ — } {}^5I_7.$$

Out of these transitions, the transitions ${}^5F_3-{}^5I_6$ and $({}^5F_4, {}^5S_2)-{}^5I_7$ have been observed for the first time in fluorescence while in the remaining transitions, more number of lines have been observed in the present study than reported by Caspers *et al* (1970). Most of the fluorescence lines are completely polarized and the rest of the partially polarized lines could be explained as due to overlapping transitions. The two fluorescence groups observed for the first time in the present study, are shown in figure 3.

Among the various wavelengths of Ar⁺ laser used for exciting the fluorescence, 4658 Å laser line coincides with the transition from the lowest Stark component of the

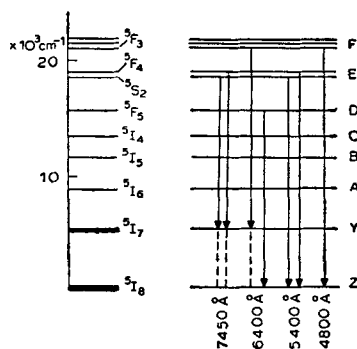


Figure 2. Partial energy level diagram of Ho³⁺ : LaF₃ showing the observed fluorescence transitions

ground state to 3K_8 state. The excitations due to other wavelengths could be phonon assisted processes. However, from the present studies it is not possible to pinpoint the actual processes responsible for exciting the ions.

6. Classification of the Stark components

The transitions corresponding to the various lines observed in the absorption spectrum are identified from the absorption data given by Caspers *et al* (1970). Further, the Stark components are classified under the irreducible representations of C_{2v} point group using the polarization features of the absorption spectrum and the selection rules given in table 1. Also, the analysis of the fluorescence spectrum has been used to confirm the assignment made for some of the Stark components from the absorption, data, while it could suggest new assignments where absorption data were insufficient in the classification of the Stark components. The latter is true, particularly, for the

Table 1. Selection rules for electric dipole transitions at rare-earth ion site in LaF₃

C_{2v}	A_1	B_1	A_1	B_2
A_1	σ	σ	—	π
B_1	σ	σ	π	—
A_2	—	π	σ	σ
B_2	π	—	σ	σ

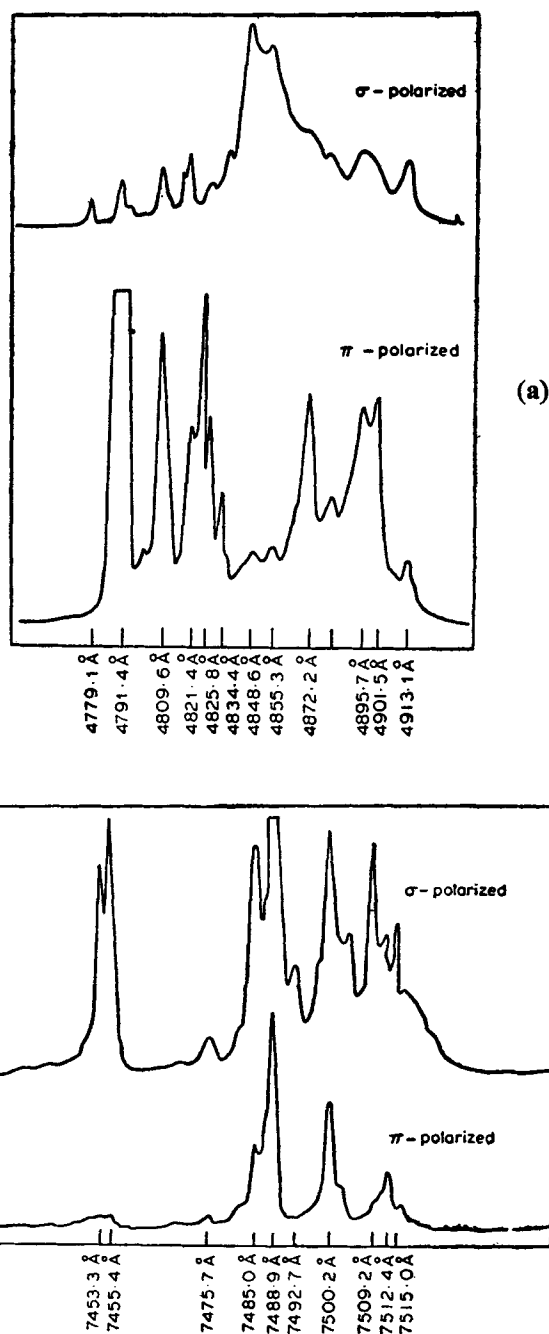


Figure 3. Ar⁺ laser excited fluorescence of Ho³⁺ : LaF₃ at 80°K (a) 4800 Å group (b) 7450 Å group.

ground state, because its higher Stark components cannot be observed in absorption. To classify the various Stark components, the following procedure is followed. As the absorption is observed only from the lowest three components, Z_1, Z_2, Z_3 of the ground

state, 5I_8 , only these along with the involved stark components of excited states are classified with the help of the absorption data. If the fluorescence included any states where absorption data are analysed, the analysis of these fluorescence groups is considered first either to confirm the assignments made or to make assignment for the unclassified Stark components. Thus, the higher Stark components of 5I_8 , are classified with the help of fluorescence terminating in them. The states not observed in absorption but in fluorescence only are analysed at the end.

Table 2. Classification of the Stark components of various states of $\text{Ho}^{3+}:\text{LaF}_3$

SLJ state	Stark component	Species (under C_{2v})	SLJ state	Stark component	Species (under C_{2v})
5G_5	J_1	A_2B_2	5F_5	D_1	A_1
	J_2	B_1		D_2	B_1
	J_3	A_2B_2		D_3	A_2B_2
	J_4	A_1		D_4	A_2B_2
	J_5	A_2B_2		D_5	A_2B_2
	J_6	A_2B_2		D_6	A_2B_2
	J_7	A_2B_2		D_7	B_1
	J_8	A_2B_2		D_8	A_2B_2
	J_9	A_1		D_9	A_1
	J_{10}	B_1		D_{10}	B_1
	J_{11}	B_1		D_{11}	A_2B_2
5G_6	I_1	A_2B_2	5I_7	Y_1	—
	I_2	A_1		Y_2	—
	I_3	A_2B_2		Y_3	—
	I_4	B_1		Y_4	—
	I_5	A_2B_2		Y_5	A_2B_2
	I_6	A_2B_2		Y_6	—
	I_7	B_1		Y_7	A_1B_2
	I_8	A_1		Y_8	—
	I_9	B_1		Y_9	A_1B_1
	I_{10}	A_1		Y_{10}	A_1B_1
	I_{11}	A_1		Y_{11}	—
	I_{12}	A_2B_2		Y_{12}	—
	I_{13}	A_2B_2		Y_{13}	—
5F_3	F_1	A_2B_2	5I_8	Y_{14}	—
	F_2	A_2B_2		Y_{15}	—
	F_3	A_1B_1		Z_1	B_2
	F_4	A_2B_2		Z_2	A_1B_1
	F_5	A_1B_1		Z_3	A_1B_1
	F_6	A_2B_2		Z_4	B_2
	F_7	A_1B_1		Z_5	A_2B_2
5F_4	E_1	A_1B_1	Z_6	A_1B_1	
	E_2	A_1	Z_7	A_1B_1	
	E_3	A_2B_2	Z_8	A_1B_1	
	E_4	A_1B_1	Z_9	A_2B_2	
	E_5	A_2B_2	Z_{10}	A_1B_1	
	E_6	A_2B_2	Z_{11}	A_2B_2	
	E_7	A_1B_1	Z_{12}	A_1B_1	
	E_8	A_1	Z_{13}	A_2B_2	
	E_9	A_2B_2	Z_{14}	A_1B_1	
5S_3	E_1°	A_2B_2	Z_{15}	A_2B_2	
	E_2°	A_1	Z_{16}	A_1B_1	
	E_3°	A_1	Z_{17}	A_2B_2	
	E_4°	A_2B_2			
	E_5°	B_1			

As mentioned earlier the fluorescence spectrum contains both completely as well as partially polarized lines. For the classification of Stark components the polarization properties of completely polarized lines only are used.

All the Stark components of the states 5G_5 , 5G_6 , 5F_3 , 5F_4 , 5S_2 , 5F_5 , and 5I_8 and a few of 5I_7 have been classified in terms of the irreducible representations of C_{2v} point group. The classification is presented in table 2.

7. Conclusions

The assumption of C_{2v} site symmetry for rare-earth ions in LaF_3 on the whole seems to be fairly valid as the polarization features of almost of all the lines in absorption and fluorescence spectra of $\text{Ho}^{3+} : \text{LaF}_3$ are satisfactorily interpreted under C_{2v} site symmetry. However, for most of the cases, it has not been possible to distinguish between A_1 and B_1 or between A_2 and B_2 and this ambiguity persists in the present classification.

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