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Optical absorption spectrum of thulium nitrate in solution

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Abstract. Spectral investigation of Tm^{3+} in thulium nitrate has been carried out. For the first time, the second derivative spectrum of this complex has been recorded. The results of a least squares fit of the energy levels and oscillator strengths of the bands are reported in terms of interaction parameters and Judd-Ofelt parameters. Radiative transition probabilities for fluorescence levels $^3P_0$, $^1I_6$, $^1D_2$ and $^1G_4$ of Tm^{3+} in thulium nitrate are estimated.

Keywords. Thulium nitrate; optical absorption; derivative spectrum; transition probabilities.

1. Introduction

Considerable progress has been made in interpreting the optical spectra of Tm^{3+} ion embedded in crystalline solids (Dieke 1968), in different solution media (Carnall *et al* 1965, 1968) and in glasses (Reisfeld 1975).

Since no detailed investigation of the optical absorption spectrum of thulium nitrate has so far been reported in literature, the authors took up the present investigation of work. For the first time, derivative spectrum of this sample has been studied by the authors.

2. Experimental

Thulium Nitrate solution of 0·1 mole percent was prepared. Normal and second derivative spectrum in the wavelength region 8300 Å–2300 Å were recorded on a Perkin-Elmer 551 recording spectrophotometer.

The near infrared spectrum in the wavelength region of 11100 Å–14300 Å was recorded on a Carl-Zeiss Specord 61 recording spectrophotometer. Second derivative spectrum could not be recorded in this region as there is no derivative accessory for this NIR instrument. The refractive index of the solution was measured on a PZO WARSZANARL Nr 3275 refractometer.

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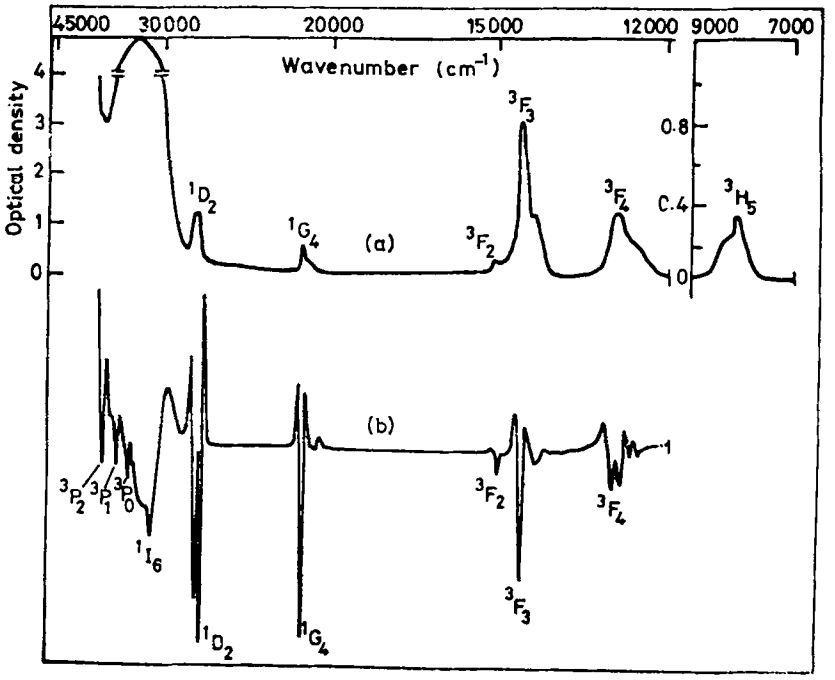

Figure 1. Absorption spectrum of thulium nitrate solution. (a) normal spectrum (b) second derivative spectrum.

3. Results and analysis

3.1. *Energy levels*

Under the influence of an electric field of the solution matrix, the changes in the parameters E^k ($k = 1, 2, 3$) and ξ_{4f} are very small. To a first order approximation therefore, the energy E_J of the Jth level may be expressed by a Taylor-series expansion as follows

$$E_J = E_{0J} + \frac{dE_J}{dE^1}\Delta E^1 + \frac{dE_J}{dE^2}\Delta E^2 + \frac{dE_J}{dE^3}\Delta E^3 + \frac{dE_J}{d\xi_{4f}}\Delta\xi_{4f} + \\ + \frac{dE_J}{da}\Delta a + \frac{dE_J}{d\beta}\Delta\beta \qquad (1)$$

where E_{0J} is the zero-order energy of the level J, and dE_J/dE^k, $dE_J/d\xi_{4f}$, dE_J/da and $dE_J/d\beta$ are the partial derivatives. Further

$$\Delta E^k = E^k - E^{k0}$$
$$\Delta\xi_{4f} = \xi_{4f} - \xi^0_{4f}$$
$$\Delta a = a - a^0$$
$$\Delta\beta = \beta - \beta^0 \qquad (2)$$

Table 1. Experimental and calculated energy levels and spectroscopic parameters for Tm^{3+} : $Tm(No_3)_3 \cdot 5H_2O$.

Energy level	E_{exp} (cm^{-1})	E_{cal} (cm^{-1})	Parameters (cm^{-1})
$^3H_4$	...	5736	$E^1 = 6533 \cdot 02$
$^3H_5$	8090	8377	$E^2 = 31 \cdot 222$
$^3F_4$	12833	12788	$E^3 = 642 \cdot 493$
$^3F_3$	14648	14675	$\xi_{4f} = 2680 \cdot 54$
$^3F_2$	15193	15089	$a = -39 \cdot 889$
$^1G_4$	21546	21531	$\beta = 405 \cdot 382$
$^1D_2$	27770	27930	
$^1I_6$	32511	32492	
$^3P_0$	35263	35483	
$^3P_1$	36686	36478	
$^3P_2$	38376	38246	
$^1S_0$	...	74743	
RMS deviation.	$\pm$ 152 cm^{-1}		

where E^{k0}, $^g\xi_f$, a_0 and β° are the free ion parameters and E^k, ξ_{4f}, a and β are the parameters of the ion in the crystal or solution matrix.

Figure 1 shows the normal and second derivative spectra of thulium nitrate. The assignments of electronic transitions to the observed bands was straight forward.

For the numerical evaluation of the E^k, ξ_{4f}, a and β parameters, the observed energy levels were substituted for E_J in (1). The values of the zero-order energies and partial derivatives were taken from the data given by Lakshman and Jayasankar (1982). With the linear equations thus formed which are equal to the number of observed levels, the values of $\triangle E^k$, $\triangle \xi_{4f}$, $\triangle a$ and $\triangle \beta$ were evaluated by the least square fit method. From these delta values, the parameters E^k, ξ_{4f}, a and β for Tm^{3+} in thulium nitrate were calculated using the formula given in (2) and ars presented in table 1. The energy levels calculated using the above parametere are presented in table 1 along with the observed band positions. The wavefunctions in the intermediate scheme are given in table 2.

3·2. *Spectral intensities and transition probabilities*

The oscillator strengths and the Judd-Ofelt parameters (T_λ and Ω_λ) are evaluated as detailed in our earlier paper (Lakshman and Jayasankar 1982) and are presented in table 3.

Table 2. Computed eigenvalues and eigenvectors for Tm^{3+} : $Tm(NO_3)_3 \cdot 5H_2O$.

Assignment from $^3H_6$	J	Eigenvalue	Eigenvector components
^3H	6	0	$0{\cdot}10156\ ^1I + 0{\cdot}99483\ ^3H$
^3H	4	5736	$-0{\cdot}28695\ ^3H + 0{\cdot}54776\ ^1G + 0{\cdot}78589\ ^3F$
^3H	5	8377	$1{\cdot}00000\ ^3H$
^3F	4	12788	$-0{\cdot}76768\ ^3H + 0{\cdot}35923\ ^1G - 0{\cdot}53068\ ^3F$
^3F	3	14675	$1{\cdot}00000\ ^3F$
^3F	2	15089	$-0{\cdot}86726\ ^3F + 0{\cdot}47633\ ^1D + 0{\cdot}14478\ ^3P$
^1G	4	21531	$0{\cdot}57301\ ^3H + 0{\cdot}75558\ ^1G - 0{\cdot}31742\ ^3F$
^1D	2	27930	$0{\cdot}45475\ ^3F + 0{\cdot}63958\ ^1D + 0{\cdot}61979\ ^3P$
^1I	6	32492	$-0{\cdot}99483\ ^1I + 0{\cdot}10156\ ^3H$
^3P	0	35483	$-0{\cdot}96980\ ^3P + 0{\cdot}24389\ ^1S$
^3P	1	36478	$1{\cdot}00000\ ^3P$
^3P	2	38246	$0{\cdot}20263\ ^3F + 0{\cdot}60336\ ^1D - 0{\cdot}77130\ ^3P$
^1S	0	74743	$0{\cdot}24389\ ^3P + 0{\cdot}96980\ ^1S$

Table 3. Experimental and calculated oscillator strengths and squared reduced matrix elements $(f^{12}\ ^3H_6 \| U^\lambda \| f^{12}\ S'L'J')^2$ for Tm^{3+}: $Tm(NO_3)_3 \cdot 5H_2O$.

$S'L'J'$	$f_{exp} \times 10^6$	$f_{cal} \times 10^6$	$(U^2)^2$	$(U^4)^2$	$(U^6)^2$
$^3H_6$	0·205	0·835	0·10722	0·23104	0·63730
$^3F_4$	1·746	1·274	0·24158	0·11109	0·60523
$^3F_3$	2·071	1·625	0	0·31588	0·83973
$^3F_2$	0·184	0·162	0	0·00002	0·25724
$^1G_4$	0·343	0·584	0·04735	0·07140	0·01389
$^1D_2$	2·634	2·180	0	0·30913	0·09402
RMS deviation	$0{\cdot}425 \times 10^{-6}$				

Refractive Index (n) = 1·3363

$T_2 = 0{\cdot}19647 \times 10^{-9}$; $T_4 = 0{\cdot}24137 \times 10^{-9}$; $T_6 = 0{\cdot}04132 \times 10^{-9}$; $\Omega_2 = 1{\cdot}97544 \times 10^{-20}$ (cm^2) ; $\Omega_4 = 2{\cdot}42690 \times 10^{-20}$ (cm^2) ; $\Omega_6 = 0{\cdot}41546 \times 10^{-20}$ (cm^2).

Table 4. Values of $(SLJ \|U^{\lambda}\| S'L'J')^2$ for Tm^{+3} : $Tm(NO_3)_3 \cdot 5H_2O$. Electric dipole linestrength (S_{ed}), Magnetic dipole linestrength (S_{md}), Total transition probability (A), Total oscillator strength (f) and the Radiative lifetime (τ_R) for Tm^{3+} : $Tm(NO_3)_3 \cdot 5H_2O$.

SLJ (1)	$S'L'J'$ (2)	$(U^2)^2$ (3)	$(U^4)^2$ (4)	$(U^6)^2$ (5)	$S_{ed}/e^2 \times 10^{22}$ (6)	$S_{md}/c^2 \times 10^{22}$ (7)	$f \times 10^6$ (8)	A (9)
$^3P_0$	$^1I_6$	0	0	0·02468	1·025	0	0·036	0
	$^1D_2$	0·02574	0	0	5·085	0	0·492	33
	$^1G_4$	0	0·04441	0	10·778	0	1·911	424
	$^3F_2$	0·36286	0	0	71·681	0	18·592	8829
	$^3F_3$	0	0	0	0	0	0	0
	$^3F_4$	0	0·02184	0	5·300	0	1·536	911
	$^3H_5$	0	0	0	0	0	0	0
	$^3H_4$	0	0·28125	0	68·257	0	26·046	26771
	$^3H_6$	0	0	0·07649	3·178	0	1·448	2123
						$A_T = 39091$, $\tau_R = 25·6\ \mu$ sec		
$^1I_6$	$^1D_2$	0	0·04915	0·83918	46·793	0	0·221	6
	$^1G_4$	0·21489	1·25563	0·62913	373·317	0	4·069	577
	$^3F_2$	0	0·04282	0·36864	25·708	0	0·443	156
	$^3F_3$	0	0·00329	0·00875	1·162	0	0·021	8
	$^3F_4$	0·06760	0·30670	0·09205	91·611	0	1·792	818
	$^3H_5$	0·00112	0·00241	0·00664	1·082	0	0·026	18
	$^3H_4$	0·06022	0·49757	0·39987	149·264	0	3·973	3358
	$^3H_6$	0·01257	0·04604	0·01590	14·317	0·57710	0·484	603
						$A_T = 5540$, $\tau_R = 180·4\ \mu$ sec.		
$^1D_2$	$^1G_4$	0·19388	0·17705	0·00102	81·310	0	1·308	60
	$^3F_2$	0·06436	0·30263	0	86·159	3·47676	2·928	546
	$^3F_3$	0·16117	0·06476	0	47·555	0	1·613	327
	$^3F_4$	0·13396	0·01331	0·23164	39·317	0	1·518	399
	$^3H_5$	0	0·00049	0·02316	1·081	0	0·055	25
	$^3H_4$	0·54629	0·09609	0·02223	132·160	0	7·527	4308
	$^3H_6$	0	0·30913	0·09402	78·929	0	5·665	5151
						$A_T = 10816$, $\tau_R = 92·5\ \mu$ sec.		
$^1G_4$	$^3F_2$	0·00455	0·06836	0·04173	19·223	0	0·175	8
	$^3F_3$	0·01029	0·07242	0·30450	32·259	0	0·320	18
	$^3F_4$	0·15855	0·00386	0·37120	47·679	11·35248	0·756	68
	$^3H_5$	0·07376	0·00554	0·54331	38·488	0	0·744	156
	$^3H_4$	0·00329	0·01981	0·07436	8·547	0·58331	0·209	62
	$^3H_6$	0·04735	0·07140	0·01389	27·259	0	0·843	462
						$A_T = 777$, $\tau_R = 1287·0\ \mu$ sec.		

The total radiative transition probability for a transition $\psi J \rightarrow \psi' J'$ is given by

$$A(\psi J : \psi' J') = \frac{64\pi^4\sigma^3}{3h(2J+1)}\left(\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md}\right) \quad (3)$$

where the symbols have their usual significance (Reisfeld 1975). Since the excited state relaxation usually involves transition to a number of states, we define a total radiative relaxation rate

$$A_T(\psi J) = \sum_{\psi' J'} A(\psi J : \psi' J') \quad (4)$$

where the sum runs over all $\psi' J'$ lower in energy than ψJ. The radiative lifetime of a state is

$$\tau_R(\psi J) = (A_T(\psi J))^{-1} \quad (5)$$

The calculated radiative lifetimes are given in table 4.

4. Discussion

The radiative lifetime for Tm^{3+} in thulium nitrate is highest in $^1G_4$, while it is least in $^3P_0$ level. Similar results have been reported in glasses also (Reisfeld 1975). Second derivative spectra exhibit (figure 1b) splittings in $^3F_4$, $^3F_3$, $^1G_4$ and $^1D_2$ levels. Since the crystal symmetry for Tm^{3+} in thulium nitrate is not clearly known, no attempt to calculate the approximate crystal field parameters could be made. It is interesting to note that the closely lying $^1I_6$, $^3P_0$, $^3P_1$ and $^3P_2$ levels are very well resolved in the second derivative spectrum as is seen in figure 1b.

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