Pramāṇa, Vol. 23, No. 2, August 1984, pp. 129–140. © Printed in India.

# Optical absorption spectra of tripositive erbium ion in certain nitrate complexes

S V J LAKSHMAN and C K JAYASANKAR
Department of Physics, S V University, Tirupati 517 502, India

MS received 16 November 1983; revised 7 May 1984

**Abstract.** Optical absorption of $Er^{3+}$ ion in $Er(NO_3)_3 \cdot 5H_2O$, $NH_4NO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $KNO_3$ and $NaNO_3$ complexes has been studied. The second derivative spectra of these $Er^{3+}$ complexes exhibited splittings in the $^4I_{9/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^2H_{9/2}$ levels. These splittings have been tentatively explained as due to a cubic crystalline field. The partial derivatives for $Er^{3+}$ ion have been calculated in terms of Racah ($E^k$) parameters. 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 various fluorescence levels are theoretically estimated. The lifetime of the $^4G_{11/2}$ level is found to be lowest in all nitrate complexes.

**Keywords.** Erbium nitrate; optical absorption; oscillator strengths; transition probability; derivative spectrum; tripositive erbium.

**PACS No. 78·50**

## 1. Introduction

Considerable progress has been made in interpreting the optical spectra of $Er^{3+}$ ion embedded in crystalline solids (Dieke 1968; Hufner 1978; Wybourne 1965; Crosswhite and Moos 1967; Chang *et al* 1982; Gruber *et al* 1982; Hayhurst *et al* 1981; Ryba-Romanowski *et al* 1980; Faulkner *et al* 1980; Mazurak *et al* 1983), in different solution media (Carnall *et al* 1965, 1968; Hoogschagen and Gorter 1948; Lakshman and Jayasankar 1984), in glasses (Reisfeld and Eckstein 1975) and in garnets (Pappalardo 1963; Koningstein and Geusic 1964).

Prandtl and Scheiner (1934) presented almost a complete collection of trivalent lanthanide solution absorption spectra. Carnall *et al* (1965) reported the absorption spectra of the trivalent lanthanides in aqueous, acid and molten solutions and correlated the experimentally observed energies and intensities with the corresponding theoretically calculated values. Krupke and Gruber (1963) reported the absorption and fluorescence spectra of $Er^{3+}$: $LaF_3$.

The theoretical interpretation of solution spectra has undergone significant advances in recent years. It is now possible to compute both the energies and intensities of bands. Optical absorption spectra of $Er(NO_3)_3 \cdot 5H_2O$ in the presence of $NH_4NO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $KNO_3$ and $NaNO_3$ complexes have so far not been reported in literature. The authors therefore recorded both the normal and second derivative spectra of these complexes.

## 2. Experimental

Saturated solutions of ammonium nitrate (AN), magnesium nitrate (MN), potassium nitrate (PN) and sodium nitrate (SN) were prepared. To each of these solutions 0·1 mole % of 4N erbium nitrate (EN) (M/s Rare Earth Products Limited, London) was added. The absorption spectra of erbium nitrate complexes were recorded in the UV-VIS region (45000 $cm^{-1}$ to 12000 $cm^{-1}$) on a Perkin-Elmer 551 recording spectrophotometer. The second derivative spectra of these complexes were also recorded in this spectral region. The IR spectra in the region from 13000 to 3000 $cm^{-1}$ and 4000 to 200 $cm^{-1}$ for EN in KBr were recorded using Carl-Zeiss Specord 61 and Pye Unicam SP3 300 IR spectrophotometers respectively. The refractive indices of the EN complexes were measured on a PZO RL Nr3275 refractometer. The experimental intensities of the bands were determined from their profiles.

## 3. Results and analysis

The normal and second derivative spectra of $Er^{3+}$ in EN, AN, MN, PN and SN solutions are shown in figures 1a to 5a and 1b to 5b respectively. The normal spectra closely resemble the spectrum of erbium aquo ion (Carnall 1979). However, the second derivative spectra (figures 1b to 5b) exhibited certain structural details, such as resolution in closely lying high energy (above 25000 $cm^{-1}$) bands and splitting of low energy bands

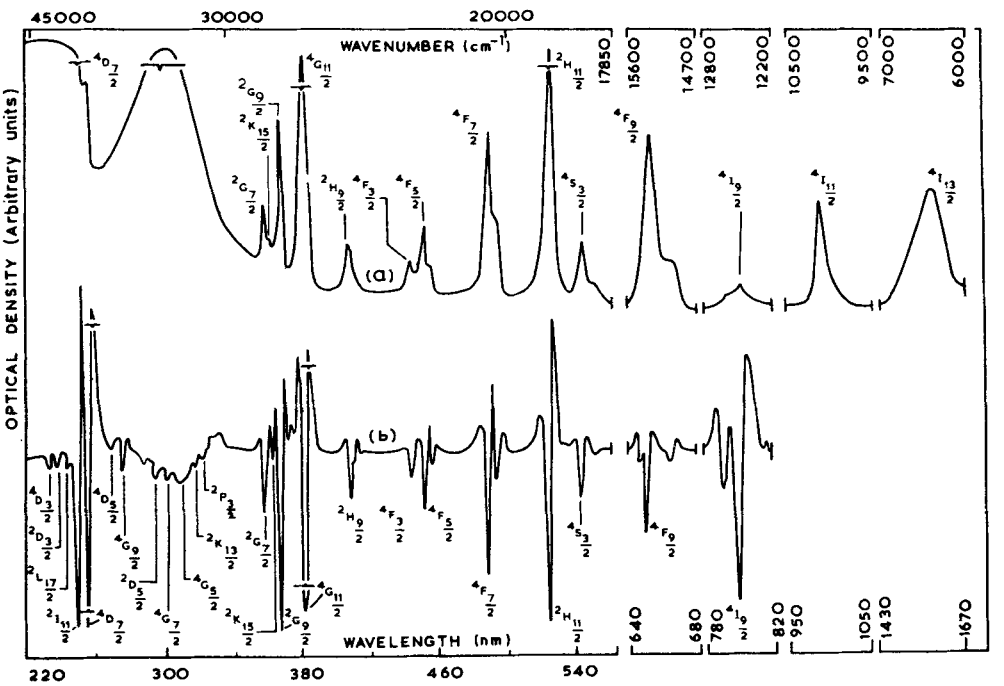


**Figure 1.** Absorption spectrum of erbium nitrate solution: (a) normal spectrum (b) second derivative spectrum.

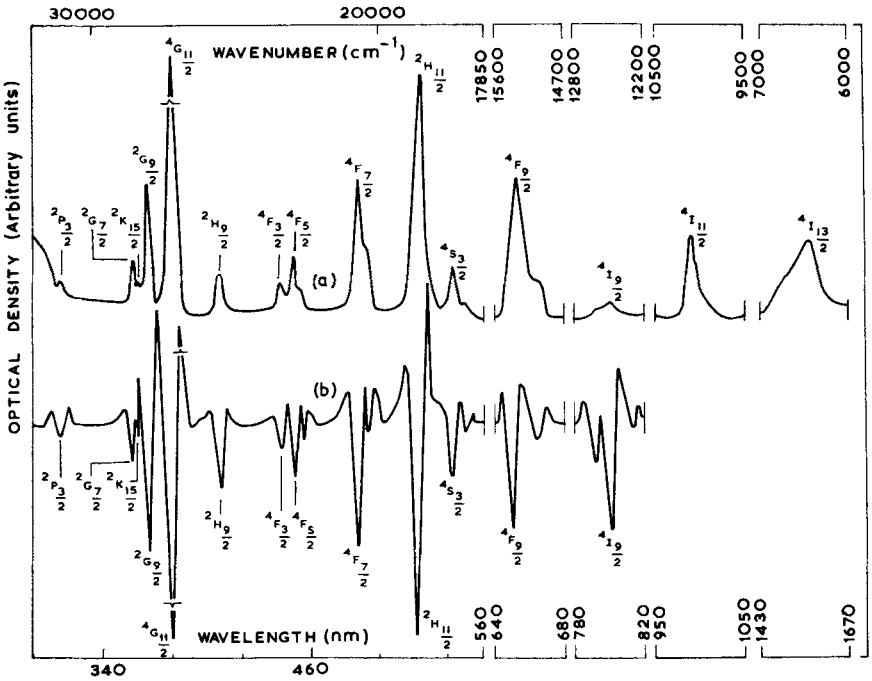


**Figure 2.** Absorption spectrum of $Er^{3+}:NH_4NO_3$: (**a**) normal spectrum (**b**) second derivative spectrum.

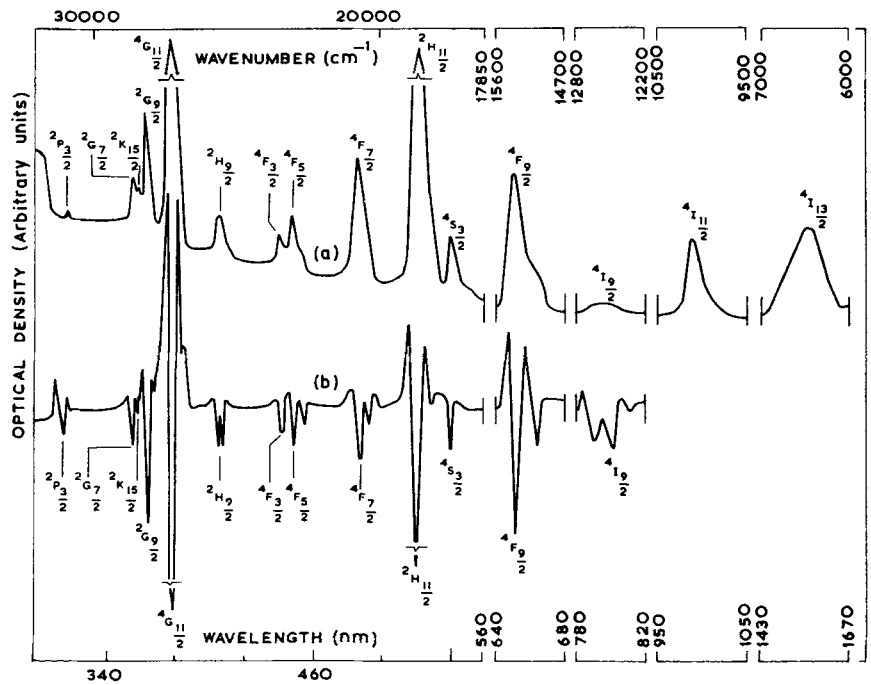


**Figure 3.** Absorption spectrum of $Er^{3+}:Mg(NO_3)_2 \cdot 6H_2O$: (**a**) normal spectrum (**b**) second derivative spectrum.

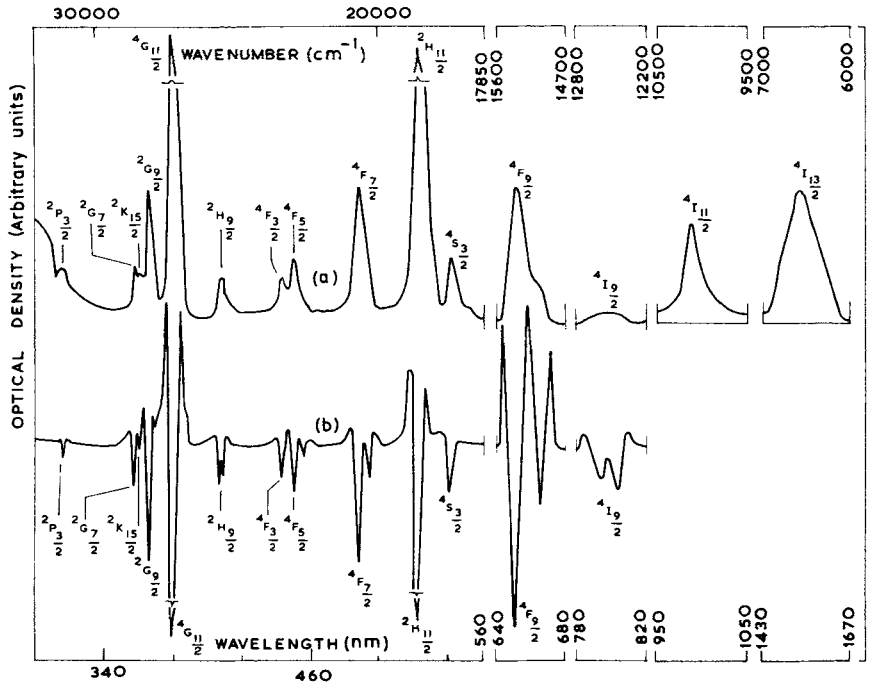


**Figure 4.** Absorption spectrum of $Er^{3+}$ : $KNO_3$: (**a**) normal spectrum (**b**) second derivative spectrum.

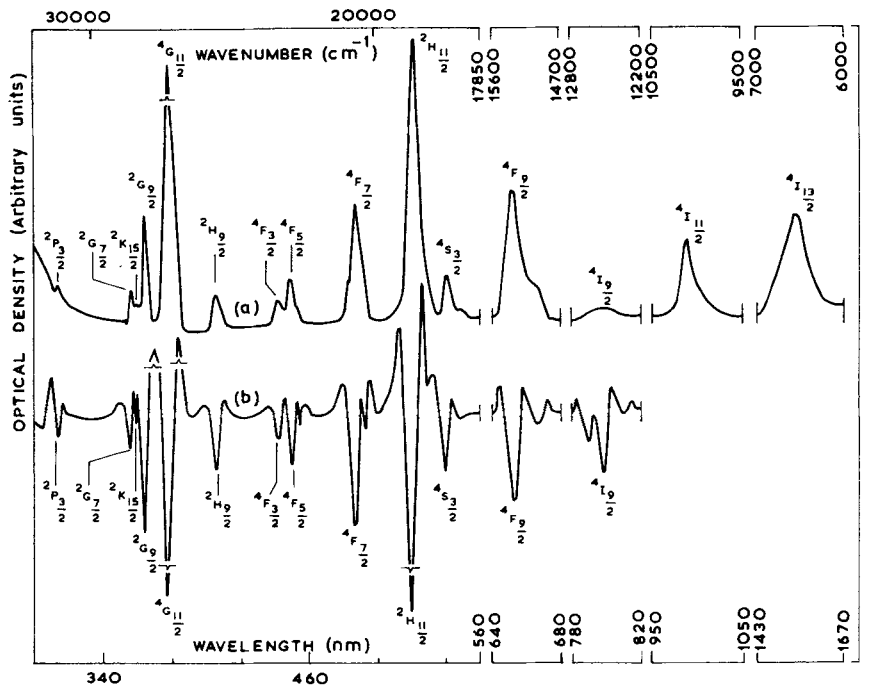


**Figure 5.** Absorption spectrum of $Er^{3+}$ : $NaNO_3$: (**a**) normal spectrum (**b**) second derivative spectrum.

and permitted the identification of high energy bands ($^2K_{15/2}$, $^2P_{3/2}$, $^4G_{5/2}$, $^4G_{7/2}$ etc.,) with certainty.

### 3.1 *Electronic energy levels*

The identification and analysis of the bands were straightforward. The wavenumbers of the observed bands are presented in table 1 along with their assignments. Under the influence of the electric field of the solution matrix, the changes in the electrostatic ($E^1$, $E^2$, $E^3$), spin-orbit ($\xi_{4f}$) and configuration interaction ($\alpha$, $\beta$, $\gamma$) parameters are very small. To a first order approximation, the energy $E_J$ of the $J$th level may be expressed in terms of the changes in the parameters $P_k$ ($P_1 = E^1$, $P_2 = E^2$, $P_3 = E^3$, $P_4 = \xi_{4f}$, $P_5 = \alpha$, $P_6 = \beta$ and $P_7 = \gamma$) by a Taylor-series expansion as follows (Wong 1961).

$$E_J = E_{0J} + \sum_{k=1}^{7} (dE_J/dP_k)\Delta P_k. \tag{1}$$

$E_{0J}$ is the zero order energy of the level $J$ and $dE_J/dP_k$ are the partial derivatives. Further

$$\Delta P_k = P_k - P_k^o, \tag{2}$$

where $P_k^o$ is the free ion parameter and $P_k$ is the parameter of the ion in the crystal or solution matrix.

Using the $E_{0J}$ values and the partial derivatives given earlier (Lakshman and Jayasankar 1984) and the experimental band positions as $E_J$ (table 1) for the respective energy levels, (1) was solved by the least squares fit method to evaluate $\Delta P_k$ values. From

**Table 1.** Experimental energy levels ($E$) and oscillator strengths ($f$) of $Er^{3+}$ ion in EN, AN, MN, PN, PN and SN nitrate complexes.

| | EN | | AN | | MN | | PN | | SN | |
|---|---|---|---|---|---|---|---|---|---|---|
| Terms | $E$ ($cm^{-1}$) | $f$ ($\times 10^{-6}$) | $E$ ($cm^{-1}$) | $f$ ($\times 10^{-6}$) | $E$ ($cm^{-1}$) | $f$ ($\times 10^{-6}$) | $E$ ($cm^{-1}$) | $f$ ($\times 10^{-6}$) | $E$ ($cm^{-1}$) | $f$ ($\times 10^{-6}$) |
| $^4I_{13/2}$ | 6390 | — | 6615 | — | 6450 | — | 6440 | — | 6560 | — |
| $^4I_{11/2}$ | 10115 | — | 10110 | — | 10100 | — | 10105 | — | 10100 | — |
| $^4I_{9/2}$ | 12465 | 0·187 | 12497 | 0·142 | 12512 | 0·121 | 12481 | 0·110 | 12489 | 0·117 |
| $^4F_{9/2}$ | 15321 | 1·656 | 15338 | 1·566 | 15357 | 1·643 | 15333 | 1·308 | 15338 | 1·531 |
| $^4S_{3/2}$ | 18428 | 0·322 | 18496 | 0·342 | 18513 | 0·465 | 18462 | 0·355 | 18507 | 0·352 |
| $^2H_{11/2}$ | 19097 | 2·419 | 19189 | 4·482 | 19207 | 4·690 | 19115 | 2·417 | 19196 | 3·374 |
| $^4F_{7/2}$ | 20507 | 1·292 | 20528 | 2·032 | 20549 | 1·879 | 20528 | 1·152 | 20537 | 1·764 |
| $^4F_{5/2}$ | 22167 | 0·471 | 22265 | 0·627 | 22315 | 0·632 | 22256 | 0·474 | 22241 | 0·475 |
| $^4F_{3/2}$ | 22593 | 0·255 | 22644 | 0·327 | 22695 | 0·437 | 22659 | 0·262 | 22644 | 0·245 |
| $^2H_{9/2}$ | 24624 | 0·606 | 24533 | 0·579 | 24593 | 0·742 | 24684 | 0·530 | 24624 | 0·571 |
| $^4G_{11/2}$ | 26274 | 4·793 | 26343 | 10·222 | 26378 | 11·311 | 26308 | 4·268 | 26364 | 7·498 |
| $^2G_{9/2}$ | 27389 | — | 27389 | — | 27465 | — | 27427 | — | 27450 | — |
| $^2K_{15/2}$ | 27731 | — | 27770 | — | 27808 | — | 27847 | — | 27785 | — |
| $^2G_{7/2}$ | 27964 | 0·499 | 28042 | 0·373 | 28082 | 0·349 | 27886 | 0·490 | 28042 | 0·405 |
| $^2P_{3/2}$ | — | — | 31586 | — | 31662 | — | 31656 | — | 31656 | — |
| RMS deviation* | ±89 | ±0.202 | ±90 | ±0·499 | ±81 | ±0·526 | ±94 | ±0·274 | ±74 | ±0·350 |

* To save space calculated values are not given.

**Table 2.** Slater-Condon, Racah, spin-orbit, configuration interaction, operator equivalent factors and crystal field parameters of $Er^{3+}$ ion in nitrate complexes (Values in $cm^{-1}$).

| Parameter | EN | AN | MN | PN | SN |
|---|---|---|---|---|---|
| $F_2$ | 442·737 | 458·667 | 452·220 | 429·060 | 446·798 |
| $F_4$ | 71·176 | 75·546 | 72·946 | 63·583 | 71·433 |
| $F_6$ | 7·589 | 8·868 | 8·196 | 6·319 | 7·892 |
| $E^1$ | 6958·4 | 7479·0 | 7212·7 | 6374·8 | 7064·0 |
| $E^2$ | 31·370 | 32·678 | 32·306 | 31·394 | 31·971 |
| $E^3$ | 650·06 | 646·55 | 650·98 | 650·58 | 648·15 |
| $\xi_{4f}$ | 2386·3 | 2417·4 | 2396·0 | 2401·3 | 2407·6 |
| $\alpha$ | 22·343 | 23·573 | 22·564 | 26·265 | 22·288 |
| $\beta$ | −859·82 | −926·90 | −876·08 | −1016·28 | −872·51 |
| $\gamma$ | −273·22 | −2574·37 | −1264·81 | 2836·75 | −625·21 |
| $\beta_J \times 10^5$ | 4·5113 | 4·5131 | 4·5115 | 4·5117 | 4·5124 |
| $\gamma_J \times 10^6$ | 2·0020 | 2·0000 | 2·0020 | 2·0020 | 2·0010 |
| $A_{40}$ | −127·4 | −111·4 | −107·5 | −130·6 | −125·8 |
| $A_{60}$ | 78·8 | 91·4 | 99·8 | 84·1 | 95·5 |

these delta values, the parameters $E^1$, $E^2$, $E^3$, $\xi_{4f}$, $\alpha$, $\beta$, and $\gamma$ for $Er^{3+}$ in EN, AN, MN, PN and SN complexes were calculated using (2) and are presented in table 2.

The RMS deviations $\pm 89$, $\pm 90$, $\pm 81$, $\pm 94$ and $\pm 74$ $cm^{-1}$ in EN, AN, MN, PN and SN complexes (table 1) are quite encouraging. The interelectronic repulsion, spin-orbit and configuration interaction parameters now obtained for $Er^{3+}$ in AN, MN, PN and SN along with the EN are also given in table 2. It is interesting that the hydrogenic ratios $F_4/F_2$ and $F_6/F_2$ ratios are each equal to 0·161 and 0·017 respectively for the $Er^{3+}$ in EN and are almost the same for the ion in different environments. This suggests that although the environment matrix changes from system to system, the radial properties of the tripositive erbium ion remain unaffected.

### 3.2 *Spectral intensities*

The oscillator strength ($f$) is expressed as

$$f = 4{\cdot}318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu, \tag{3}$$

where $\varepsilon(\nu)$ is the molar extinction coefficient corresponding to the energy of the transition $\nu$. The molar absorbitivity at a given energy is computed from the Beer-Lambert law

$$\varepsilon = (1/Cl) \log (I_0/I), \tag{4}$$

where $C$ is the concentration of the substance in moles/litre, $l$ is the light path in the solution (cm) and $\log (I_0/I)$ is the absorbitivity or optical density which is directly read from the instrument. $d\nu$ is the bandwidth at half height at energy $\nu$.

The observed oscillator strengths, calculated using Judd-Ofelt theory (Carnall *et al* 1965), for $Er^{3+}$ ion in EN, AN, MN, PN and SN complexes are presented in table 1. The small RMS deviations obtained between the observed and calculated values (table 1) support the validity of the Judd-Ofelt theory. The refractive indices ($n$) and the Judd-Ofelt intensity parameters $T_\lambda$ and $\Omega_\lambda$ for the complexes studied are presented in table 3.

**Table 3.** Refractive index ($n$) and Judd-Ofelt intensity parameters ($T_\lambda$ and $\Omega_\lambda$) for $Er^{3+}$ ion in different nitrate complexes.

| | Complex | | | | |
|---|---|---|---|---|---|
| | $Er^{3+}$:$Er(NO_3)_3 \cdot 5H_2O$ | $Er^{3+}$:$NH_4NO_3$ | $Er^{3+}$:$Mg(NO_3)_2 \cdot 6H_2O$ | $Er^{3+}$:$KNO_3$ | $Er^{3+}$:$NaNO_3$ |
| $n$ | 1·3362 | 1·4117 | 1·4008 | 1·3602 | 1·3883 |
| $T_2 \times 10^9$ | 0·0709 | 0·2815 | 0·3089 | 0·0868 | 0·1807 |
| $T_4 \times 10^9$ | 0·1961 | 0·1624 | 0·1732 | 0·1466 | 0·1654 |
| $T_6 \times 10^9$ | 0·0490 | 0·0927 | 0·0878 | 0·0511 | 0·0763 |
| $\Omega_2 \times 10^{20}$ ($cm^2$) | 0·8774 | 3·3081 | 3·6580 | 1·0571 | 2·1586 |
| $\Omega_4 \times 10^{20}$ ($cm^2$) | 2·4269 | 1·9085 | 2·0510 | 1·7853 | 1·9758 |
| $\Omega_6 \times 10^{20}$ ($cm^2$) | 0·6064 | 1·0894 | 1·0397 | 0·6223 | 0·9115 |

### 3.3 *Hypersensitive transitions*

For $Er^{3+}$ ion, $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transitions are the hypersensitive transitions (Peacock 1975). The oscillator strengths and intensity parameter ($T_2$) of these transitions are as follows:

| | | $f \times 10^6$ | |
|---|---|---|---|
| Complex | $T_2 \times 10^9$ | $^4I_{15/2} \rightarrow {}^2H_{11/2}$ | $^4I_{15/2} \rightarrow {}^4G_{11/2}$ |
| MN | 0·3089 | 4·690 | 11·311 |
| AN | 0·2815 | 4·482 | 10·222 |
| SN | 0·1807 | 3·374 | 7·498 |
| PN | 0·0868 | 2·457 | 4·968 |
| EN | 0·0709 | 2·419 | 4·793 |

As can be seen, the oscillator strengths of these hypersensitive transitions decrease with the decrease of $T_2$ parameter which is in accordance with the theory (Peacock 1975). The intensities of these hypersensitive transitions are highest in MN indicating greater involvement of the $f$ orbitals of $Er^{3+}$ ion in MN than in the other complexes.

### 3.4 *Radiative lifetimes*

Stein and Wurzberg (1975) pointed out that $^4F_{9/2}$ is the highest non-fluorescent level and $^4S_{3/2}$ is the lowest fluorescent level in perchlorate solution of $Er^{3+}$. Radiative lifetimes for $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^2H_{9/2}$ and $^4G_{11/2}$ excited states have been theoretically evaluated (Reisfeld 1975; Lakshman and Jayasankar 1984) and presented in table 4.

It is interesting that the lifetime of the $^4G_{11/2}$ level is least in all complexes and $^4I_{11/2}$ level is highest in EN, AN, PN and SN while that of $^4I_{13/2}$ is highest in MN. This clearly reveals that the lifetime of each fluorescent level behaves differently in different environments. For example, the lifetime of the $^4S_{3/2}$ is highest in EN and least in AN, whereas that of $^4F_{9/2}$ is highest in PN and least in MN. The lifetime variations found for the different levels in different environments are as follows:

$^4G_{11/2}$ : PN > EN > SN > AN > MN,

$^2H_{9/2}$ : PN > EN > SN > MN > AN,

$^4F_{5/2}$ : PN > EN > SN > MN > AN,

$^4F_{7/2}$ : PN > EN > SN > MN > AN,

$^4S_{3/2}$ : EN > PN > SN > MN > AN,

$^4F_{9/2}$ : PN > EN > SN > AN > MN,

$^4I_{9/2}$ : PN > EN > SN > MN > AN.

$^4I_{11/2}$ : EN > PN > SN > MN > AN,

$^4I_{13/2}$ : EN > PN > SN > MN > AN.

## 4. Discussion

The normal spectrum for $Er^{3+}$ in EN in figure 1a exhibits two broad bands at 33000 $cm^{-1}$ and 42000 $cm^{-1}$. These bands exhibited structural details in the second derivative spectrum as shown in figure 1b. From the theoretically evaluated band positions, the resolved components of high energy bands (in the second derivative spectrum) have been identified as electronic levels. These are presented in table 5.

The absorption spectrum of EN is recorded in the wavenumber region of 45000 $cm^{-1}$ to 3000 $cm^{-1}$. However, the spectra of $Er^{3+}$ in AN, MN, PN and SN were recorded only up to 32000 $cm^{-1}$ since beyond this region no bands could be observed due to abnormal noise. Carnall *et al* (1965) also made similar observation in the nitrate complexes.

The second derivative spectra (figures 1b to 5b) showed splittings for some low energy bands. They may be due to (a) impurity (b) another ionic species (c) superposition of vibronic modes of ligands on electronic levels or (d) crystal (ligand) field. Since a very pure form of erbium nitrate is used and the hosts are also analar samples (99·99 %), the first possibility is ruled out. The second possibility is also ruled out as the erbium atom is not stable in any ionic state other than $Er^{3+}$ (Dieke 1968;

**Table 4.** Predicted lifetimes for the fluorescent levels of $Er^{3+}$ ion in certain nitrate complexes (Values in $\mu$sec).

| | Complex | | | | |
|---|---|---|---|---|---|
| | EN | AN | MN | PN | SN |
| $^4G_{11/2}$ | 160 | 76 | 70 | 169 | 104 |
| $^2H_{9/2}$ | 572 | 412 | 415 | 637 | 480 |
| $^4F_{5/2}$ | 815 | 537 | 540 | 873 | 630 |
| $^4F_{7/2}$ | 536 | 404 | 404 | 601 | 455 |
| $^4S_{3/2}$ | 1597 | 772 | 812 | 1490 | 958 |
| $^4F_{9/2}$ | 1351 | 1276 | 1192 | 1658 | 1339 |
| $^4I_{9/2}$ | 6452 | 4274 | 4630 | 6993 | 5025 |
| $^4I_{11/2}$ | 23256 | 10870 | 11236 | 21277 | 13889 |
| $^4I_{13/2}$ | 18182 | 10417 | 11628 | 17241 | 12500 |

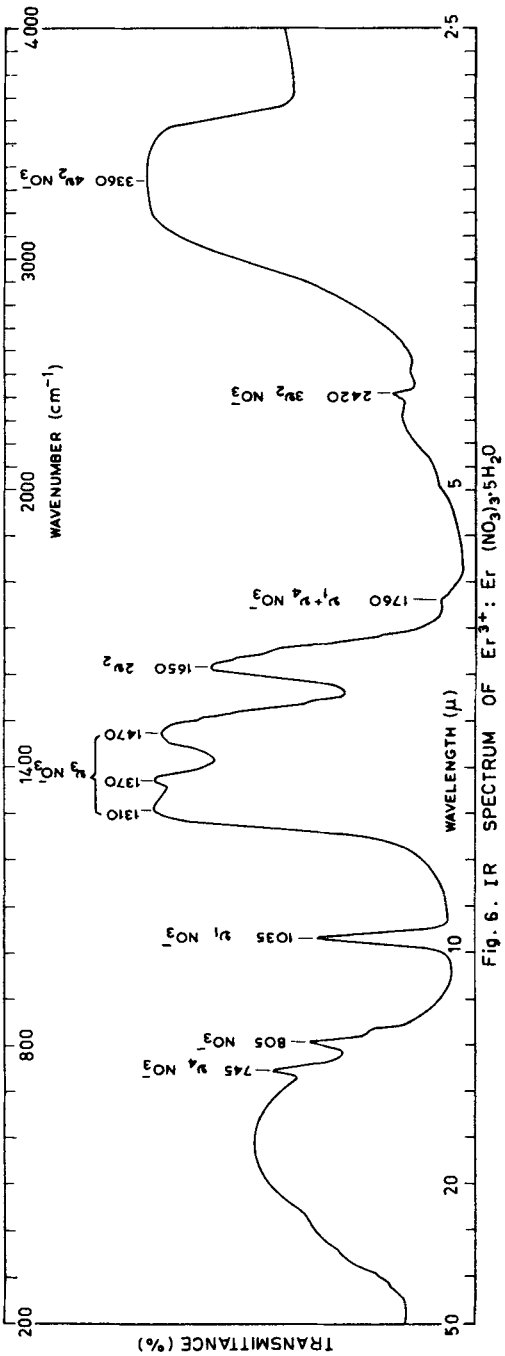


Fig. 6. IR SPECTRUM OF $Er^{3+}$: Er $(NO_3)_3 \cdot 5H_2O$

**Figure 6.** IR spectrum of $Er^{3+}$: $Er(NO_3)_3 \cdot 5H_2O$.

**Table 5.** Term assignments for components of broad bands resolved in the second derivative spectrum of $Er^{3+}$: EN.

| | Band positions ($cm^{-1}$) | | |
|---|---|---|---|
| | Observed | | |
| Term | Normal | Second derivative | Calculated* |
| $^2P_{3/2}$ | | 31380 | 31703 |
| $^2K_{13/2}$ | | 31818 | 33042 |
| $^4G_{5/2}$ | | 32734 | 33374 |
| $^4G_{7/2}$ | 33000 | 33539 | 34022 |
| $^2D_{5/2}$ | | 34269 | 34427 |
| $^4G_{9/2}$ | | 36602 | 36578 |
| $^4D_{5/2}$ | | 37476 | 38655 |
| $^2I_{11/2}$ | | 40052 | 40982 |
| $^2L_{17/2}$ | 42000 | 41352 | 41473 |
| $^2D_{3/2}$ | | 42385 | 42098 |
| $^4D_{3/2}$ | | 43103 | 43000 |

* The wide deviations between observed and calculated values in some cases may be due to the use of spectroscopic parameters ($E^k$, etc.,) obtained from low energy bands.

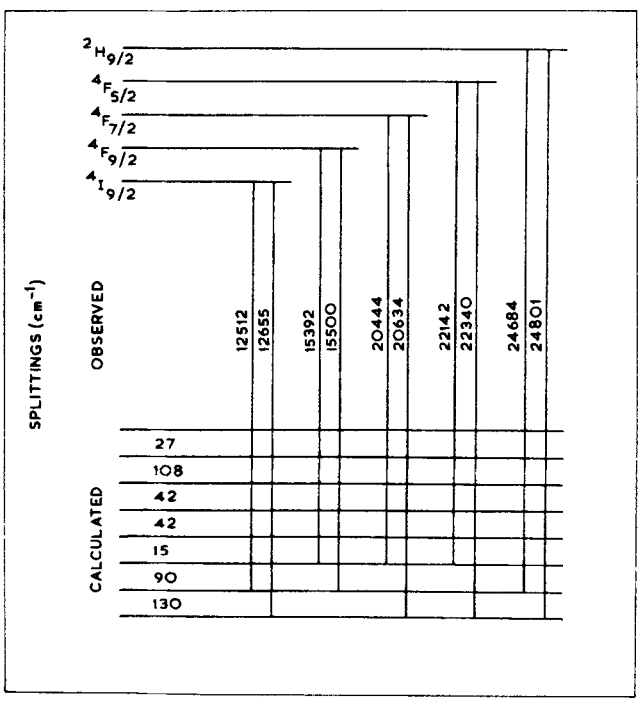


**Figure 7.** Energy level diagram showing observed transitions and calculated splittings for $Er^{3+}$ in EN.

**Table 6.** Observed and calculated crystal field splittings of $Er^{3+}$ complexes in cubic symmetry assumption (values in $cm^{-1}$).

| | EN | | AN | | MN | | PN | | SN | |
|---|---|---|---|---|---|---|---|---|---|---|
| | OBS. | CAL. | OBS. | CAL. | OBS. | CAL. | OBS. | CAL. | OBS. | CAL. |
| $^2H_{\frac{9}{2}}$ | 117 | 130 | 135 | 145 | 154 | 156 | | | | |
| $^4F_{\frac{5}{2}}$ | 198 | 220 | 237 | 215 | 247 | 219 | 238 | 229 | 248 | 235 |
| $^4F_{\frac{7}{2}}$ | 190 | 220 | 199 | 215 | 190 | 219 | 220 | 229 | 221 | 235 |
| $^4F_{\frac{9}{2}}$ | 108 | 90 | | | | | | | | |
| $^4I_{\frac{9}{2}}$ | 143 | 130 | 151 | 145 | 159 | 156 | 138 | 138 | 153 | 153 |

Hufner 1978). The vibrational modes due to $NO_3^-$ radical (Herzberg 1954) are also indicated in the IR spectra shown in figure 6. The third possibility may also be ruled out since the observed splittings in the second derivative are in no way comparable with the observed IR frequencies of figure 6.

In view of the limited IR data reported in literature and since the authors do not have access to far IR (below 200 $cm^{-1}$) instruments, the observed splittings are tentatively assumed to be due to a crystal field. The analysis presented is approximate and purely tentative.

The observed splittings are analysed by assuming cubic symmetry as detailed in our recent paper (Lakshman and Jayasankar 1984). The operator equivalent factors ($\beta_J$ and $\gamma_J$) for the ground state ($^4I_{15/2}$) of $Er^{3+}$ ion in different complexes have been evaluated and presented in table 2 along with the crystal field parameters ($A_{40}$ and $A_{60}$) following Lakshman and Jayasankar (1984). The energy level diagram showing the observed transitions and the calculated spacings is shown in figure 7 for $Er^{3+}$ in EN. The final results showing the observed and calculated splittings are presented in table 6.

## Acknowledgements

One of the authors (CKJ) thanks DST and CSIR (India) for award of fellowships.

## References

Carnall W T 1979 *Handbook on the physics and chemistry of rare earths* (New York: North Holland) Vol 3
Carnall W T, Fields P R and Rajnak K 1968 *J. Chem. Phys.* **49** 4424

Carnall W T, Fields P R and Wybourne B G 1965 *J. Chem. Phys.* **42** 3797
Chang N C, Gruber J B, Leavitt R P and Morrison C A 1982 *J. Chem. Phys.* **76** 3877
Crosswhite H M and Moos H W 1967 *Optical properties of ions in crystals* (New York: Interscience)
Dieke G H 1968 *Spectra and energy levels of rare earth ions in crystals* (New York: Interscience)
Faulkner T R, Morley J P, Richardson F S and Schwartz R W 1980 *Mol. Phys.* **40** 1481
Gruber J B, Chirico R D and Westrum Jr. E F 1982 *J. Chem. Phys.* **76** 4600
Hayhurst T, Shalimoff G, Edelstein N, Boatner L A and Abraham M M 1981 *J. Chem. Phys.* **74** 5449
Herzberg G 1954 *Molecular spectra and molecular structure II, infrared and Raman spectra of polyatomic molecules* (New York: D. Van Nostrand)
Hoogschagen J and Gorter C J 1948 *Physica* **14** 197
Hufner S 1978 *Optical Spectra of transparent rare earth compounds* (New York: Academic Press)
Koningstein J A and Geusic J E 1964 *Phys. Rev.* **136** A726
Krupke W F and Gruber J B 1963 *J. Chem. Phys.* **39** 1024
Lakshman S V J and Jayasankar C K 1984 *Spectrochimica Acta*
Mazurak Z, Hanuza J, Hermanowicz K, Jezowska-Trzebiatowska B, Schultze D and Waligora Ch 1983 *J. Chem. Phys.* **79** 255
Pappalardo R 1963 *Z. Phys.* **173** 374
Peacock R D 1975 *Struct. Bonding* **22** 83
Prandtl W and Scheiner K 1934 *Zeit. Anorg. Allgem. Chem.* **220** 107
Reisfeld R 1975 *Struct. Bonding* **22** 123
Reisfeld R and Eckstein Y 1975 *J. Chem. Phys.* **63** 4001
Ryba-Romanowski W, Mazurak Z, Jezowska-Trzebiatowska B, Schultze D and Waligora Ch 1980 *Phys. Status Solidi* **A62** 75
Stein G and Wurzberg E 1975 *J. Chem. Phys.* **62** 208
Wong E Y 1961 *J. Chem. Phys.* **35** 544
Wybourne B G 1965 *Spectroscopic properties of rare earths* (New York: Interscience)