CALCULATION OF SPECTROSCOPIC PARAMETERS FOR ERBIUM ION IN $CaWO_4$

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(*Received 6 December 1978; after revision 23 February 1979*)

The values of the inter-electronic repulsion and Lande spin-orbit parameters as well as configurational interaction parameters have been evaluated from the reported spectral data of Erbium in Calcium Tungstate crystal. The nature of the bonding in the crystal has been suggested as ionic from the magnitude of the bonding parameter.

INTRODUCTION

AN absorption spectrum of Erbium in Calcium Tungstate crystal at liquid oxygen temperature has been reported by Narasimham and Premasundaran (1971). These authors however, neither gave adequate interpretation of the nature of the transitions involved nor evaluated any ionic parameters. In the present paper, the authors therefore calculated Slater (F_k), Racah (E^k), Lande (ξ_{4f}) configurational interaction (α, β, Y (22,1)) and bonding ($b^{1/2}$) parameters after assigning energy states for the spectral lines reported by Narasimham and Premasundaran (1971).

THEORY

The energy level structure of the $4f^N$ configuration may be considered to arise from electrostatic and magnetic interactions between the $4f$ electrons. The electrostatic interaction energy E_e can be expressed in terms of Slater (F_k) parameter as follows :

$$E_e = \sum_{k=2}^{6} f^k F_k, \qquad \ldots(1)$$

where k is even and f^k's are the coefficients of the linear combination and represent the angular part of the interaction. The Slater integrals F_k are given by

$$F_k = D_k^{-1} \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R^2(r_1)\, R^2(r_2) \mathrm{d}r_1 \mathrm{d}r_2, \qquad \ldots(2)$$

where the subscripts 1, 2 are referred to electrons 1 and 2 respectively. R is the $4f$ radial wave function, $r_<$ denotes the radius of electron nearer the nucleus and $r_>$ denotes the radius of more distant electron, D_k denotes the denominator whose values are given by Condon and Shortley (1957). The Racah parameters E^k given in terms of Slater parameter F_k are shown below :

$$E^1 = \frac{70\,F_2 + 231\,F_4 + 2002\,F_6}{9}$$

$$E^2 = \frac{F_2 - 3F_4 + 7F_6}{9}$$

$$E^3 = \frac{5F_2 + 6F_4 - 91F_6}{3} \qquad \ldots(3)$$

The spin-orbit interaction energy E_{so} is given by

$$E_{so} = A_{so}\,\xi_{4f}, \qquad \ldots(4)$$

where A_{so} represents the angular part of the spin-orbit interaction and ξ_{4f} is the radial integral known as Lande parameter, The nephelauxetic ratio β is given by

$$\beta = \frac{F_k^c}{F_k^f} \qquad \ldots(5)$$

where F_k^c and F_k^f refer to the complex and the free ion respectively. The bonding parameter $b^{1/2}$ is given by

$$b^{1/2} = \left(\frac{1-\beta}{2}\right)^{\frac{1}{2}} \qquad \ldots(6)$$

Parameter Analysis

Dieke (1968)studied the absorption and fluorescence spectrum of Er^{3+} doped in $LaCl_3$ crystal and established its energy levels in the lower ground and upper states.

The assignments of the electronic energy states for the absorption lines of Erbium in Calcium Tungstate crystal have been reported by Narasimham and Premasundaran (1971). The energy E_j of the j^{th} level can be written in Taylor series expansion as

$$E_j = E_{oj} + \sum_{k=1}^{8} \frac{dE_j}{dP_k} \triangle P_k, \qquad \ldots(7)$$

where E_{oj} is the zero-order energy of the jth level $\triangle P_k$'s are the changes to be effected in the free ion parameters F_2, F_4, F_6, ξ_{4f}, α, β, $Y(22,1)$ and $Y(22,3)$. The free ion (represented with a superscript 'o') and crystal parameters are related to $\triangle P_k$'s as shown below :

$$\begin{aligned} F_k &= F_k^o + \triangle F_k \\ \xi_{4f} &= \xi^o_{4f} + \triangle \xi_{4f} \\ \alpha &= \alpha^o + \triangle \alpha \\ \beta &= \beta^o + \triangle \beta \\ Y(22,1) &= Y^o(22,1) + \triangle Y(22,1) \\ Y(22,3) &= Y^o(22,3) + \triangle Y(22,3) \end{aligned} \qquad \ldots(8)$$

The linear and non-linear theories of configurational interactions have been developed by Rajnak and Wybourne (1963) and Rajnak (1965). The parameters α and β arise from the linear configurations which differ from f^N in quantum numbers of two electrons while the non-linear parameters $Y(22,1)$, $Y(22, 3)$ arise from the interactions of the other configurations which differ from f^N configuration in quantum numbers of one electron. The values of the zero-order parameter (E_{oj}) and the partial derivatives (dE_j/dP_k) in eqn. (7) are taken from Narayana (1969). The average value of

the different components observed at each electronic energy level was used for E_j. A least square fit was carried out to calculate ΔP_k values. Using Gauss method (Scarborough (1966)), the ΔP_k parameters have been evaluated. From free ion values of F_2°, F_4°, F_6°, ξ_{4f}° etc., crystal parameters F_2, F_4, F_6, ξ_{4f} and $Y(22,1)$ have been evaluated using equations in 8. The r.m.s. deviation is calculated from the formula :

$$\sigma = \left(\frac{\sum \Delta_i^2}{N} \right)^{1/2} \qquad \ldots(9)$$

where Δ_i is the deviation of ith level and N is the number of levels fitted.

Results and Discussion

The experimental and calculated values of the energy levels for Erbium ion in $CaWO_4$ are given in Table I. The various evaluated parameters alongwith the free ion values are listed in Table II. The results are quite encouraging as the r.m.s. deviation is reasonably low.

Table I

Experimental and calculated energy levels for Er^{3+} in $CaWO_4$ crystal

Energy Level	$E_{exp.}$	$E_{cal.}$	$E_{exp.}-E_{cal.}$
	cm^{-1}	cm^{-1}	cm^{-1}
$^4F_{9/2}$	15241	15277	—36
$^4S_{3/2}$	18363	18352	11
$^2H_{11/2}$	19142	19080	62
$^4F_{7/2}$	20548	20505	43
$^4F_{5/2}$	22093	22136	—43
$^4F_{3/2}$	22398	22443	—45
$^2H_{9/2}$	24567	24563	4
$^4G_{11/2}$	26331	26377	—46
$^2K_{15/2}$	27379	27403	—24

Since the value of β is more than one, the value of $b^{1/2}$ would be imaginary. This fact therefore leads to the conclusion that the nature of the bonding is ionic for Erbium in $CaWO_4$ crystal.

TABLE II

Computed values of various parameters of erbium in $CaWO_4$ crystal

Parameter	Erbium*: Free-Ion cm^{-1}	Erbium : $CaWO_4$ cm^{-1}
F_2	442.93	437.63
F_4	68.51	68.60
F_6	7.67	7.75
ξ_{4f}	2366.50	2401.07
α	17.89	11.12
β	—7420.00	—7430.00
$Y(22,1)$	—4250.00	—4249.00
E^1	6909.58	6889.63
E^2	32.34	31.79
E^3	642.58	631.33
F_4/F_2	0.1546745	0.1567500
F_6/F_2	0.0173165	0.0177212
$\beta[F_k^c/F_k^f]$	—	1.0001500
$b^{1/2}$	—	Imaginary
The r.m. s. deviation		38.97

*Narayana, P. A. (1969)

ACKNOWLEDGEMENTS

One of the authors (S.B.) is grateful to the U.G.C. (New Delhi) for a Junior Research Fellowship.

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