

ELECTROSTATIC ENERGY MATRICES FOR $4f^5(^6PFH)5d$ SUB - CONFIGURATION OF Sm^{2+} IONS IN OCTAHEDRAL CYRSTAL FIELD

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ABSTRACT

In this paper, the problem of the interaction of the $4f^n$ and $5d$ electrons of divalent samarium Sm^{2+} , in crystalline environment is discussed within the frame work of the Yanase - Kasuya coupling formalism and the Racah irreducible tensor operator techniques. Accordingly the reduced matrix elements of the symmetric many - electron double tensor operators $V^{(1k)}$ of rank $(1,k)$, $k = 0,1,2,\dots,6$, between SL - Coupled wave functions of the $4f^5(^6PFH)$ sub -configuration are calculated and presented. In additions the block coefficient W introduced to take care of the effect of the crystalline environment on the electronic wave -functions of the $4f^5(^6PFH)5d$ sub -configuration are also computed. With these the direct Coulomb and exchange matrices are computed and their elements expressed in terms of Slater - Condon parameters $F_k(4f,5d)$, $k = 2, 4$ and $G_k(4f, 5d)$, $k = 1, 3, 5$.

1. INTRODUCTION

The free ion states of the first excited configuration $4f^55d$ of divalent samarium, Sm^{III} , (or Sm^{2+} ions) are complex. Dupont [1] has observed thousands of emission lines of Sm^{III} but has only been able to make definite level assignment to the $4f^6(^7F)$ ground multiplet and to 36 of the septet levels of $4f^5(^6PFH)5d$ sub -configuration. In free space, this sub-configuration consists of 26 multiplet in SL - coupling scheme which give rise to 140 free ion energy levels. Definite level assignment to the 36 identified septets show that the energy levels of the $4f^5(^6PFH)5d$ sub configuration of Sm^{III} range from $26\ 283.55cm^{-1}$ to $53\ 149.58cm^{-1}$ relative to the $4f^6(^7F_0)$ ground state [1,2].

It is expected that in crystalline environment these energy levels will be lowered relative to the ground state, making it possible for inter - electronic transitions of the type $4f_6 \leftrightarrow (^6PFH)5d$ to be observed in absorption or fluorescence for Sm^{2+} ions in crystals. In this respect it has to be noted that the lowest of the strong broad bands in the absorption spectra of Sm^{2+} ions in CaF_2 Sm^{2+} crystals at 4.2K which are ascribable to $4f^6 \rightarrow 4f^55d$ transitions lie between 15387 and $16420cm^{-1}$ relative of the $4f^6(^7F_0)$ ground state [3]. The location of corresponding bands in the absorption spectral of Sm^{2+} ions in other alkaline - earth flouride and alkali halide crystals are not markedly different [4-6].

Detailed theoretical studies of the electronic energy spectrum of the $4f^55d$ configuration of Sm^{2+} ions in crystals have proved as difficult as those of the free

ions Yanase [7] has made a bold attempt by adopting the Yanase – Kasuya coupling scheme [8] in analysing and interpreting the absorption spectra of Sm^{2+} ions in CaF_2 , SrF_2 and BaF_2 crystals. In that coupling formalism, it assumed that the states of the lone 5d electron of the first excited configuration $4f^n 5d$ ($1 \leq n \leq 13$) of rare – earth ions is strongly perturbed by the crystal potential. As a result, the SL – coupling scheme cannot be strictly applied to that configuration. However, the coupling of the states of the $4f^n$ core sub-configuration approximates to SL – coupling scheme provided one considers only states of highest spin multiplicity [7,8]. If therefore s_1 is the total spin angular momentum associated with the low – lying multiplets of the $4f^n$ sub – configuration, and s is the spin angular momentum of the 5d electron, then the total spin angular momentum, S_2 associated with coupled states is $S_2 = S_1 + s$. The composite angular momentum then becomes $J_2 = S_2 + L_1$, where L_1 is the total orbital angular momentum of the $4f^n$ electron. Accordingly, S_2 and J_2 are fairly good quantum number [7,8].

One of the high points in the theoretical analysis and interpretation of the spectra associated with $4f^{n+1} \rightarrow 4f^n 5d$ transitions of divalent rare – earth ions has been in the computation of the energies of the electrostatic perturbation interaction Hamiltonian, $H_{e1}(f,d)$ acting between the $4f^n$ and 5d electrons [7-10]. In applying the Yanase – Kasuya coupling scheme, Yanase [7] assumes that Hund's rule is applicable to the states of the $4f^n$ core sub – configuration which have the highest spin multiplicity. This assumption as well as the use of Racah – type expansion [11 – 13] of $H_{e1}(f,d)$ Hamiltonian results in the partition of $H_{e1}(f,d)$ into multipole – type Coulomb interaction operator and the anisotropic exchange and isotropic exchange interaction operators. The further assumption that the Coulomb interactions almost cancel out the anisotropic exchange interactions means that the effective $H_{e1}(f,d)$ interaction is the nearly isotropic exchange interactions between the $4f^n$ and the 5d electrons [7,8]. Consequently, the scalar products $V_f^{(1k)} \cdot V_d^{(k)}$, of the symmetric many – electron double tensor operators $V_f^{(1k)}$ and the irreducible unit double tensor operators $V_d^{(1k)}$ appearing in the expansion of $H_{e1}(f,d)$ are replaced with the scalar products $U_f^{(1k)} \cdot u_d^{(k)}$, of the symmetric many – electron tensor operator $U_f^{(1k)}$ and the irreducible unit tensor operator $u_d^{(k)}$. This strategy greatly simplifies the computation of the energy metrics since it avoids the calculation of the reduced matrix elements RME's of $V_f^{(1k)}$, of rank (1,k) between SL coupled wave functions of the $4f^n$ – core sub – configuration. These calculations are usually difficult and tedious and tables of these RME's are not easily available in literature. The approximations noted above are however made at a cost, since the procedure only leads to the fitting of the gross features of the first four broad absorption bands of Sm^{2+} ions in CaF_2 , SrF_2 and BaF_2 crystals of the theoretical

$$O_r^k(f,d) = D_r O_r^k(f,d) \quad \dots (6a)$$

Where $F_k(f,d)$ and $G_k(f,d)$ are Slater - Condon integrals and are connected with the Slater integrals [17], and

$$H_{el}(f,d) = \sum_{k=0}^{\infty} [O_r^k(f,d)F_k(f,d) + O_g^k(f,d)G_k(f,d)] \quad \dots (5)$$

The effective Hamiltonian for the direct and exchange interactions can now be written as

{ ... } in Eqns. (3) and (4) are respectively the Wigner's 3-j and 6-j symbols [16].

[10,11,15,16]. The symbols with six elements enclosed in brackets ... and tensor operators of rank, k , acting on the orbital subspaces of the 5d electron. The operators $V_{(1k)}^j$ are the symmetric many-electron double tensor operators of rank $(1,k)$ which act on the spin and orbital subspaces of the n equivalent electrons of the 4f sub-shell while $V_{(1r)}^p$ are the irreducible unit double tensor operators acting on both the spin and orbital subspaces of the 5d electron

$$O_{gk}^r(f,d) = (-1)^k (35) \begin{pmatrix} 3 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} \sum_{r=0}^4 (-1)^r (2r+1) \begin{Bmatrix} 2 & 2 & k \\ 3 & 3 & r \end{Bmatrix} \left[U_{(r)}^j \cdot u_{(r)}^p + 4V_{(1r)}^j \cdot v_{(1r)}^p \right] \quad \dots (4)$$

while the effective exchange operators can be written as

$$O_r^k(f,d) = (-1)^k (35) \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} U_{(k)}^j \cdot u_{(k)}^p \quad \dots (3)$$

The direct Coulomb operators are of the form [16].
to be redefined in terms of effective direct Coulomb and exchange operators.
 $F_k^r(f,d)$ and $G_k^r(f,d)$ is usually difficult. To overcome this difficulty, $H_{el}(f,d)$ has
Because of the need to use antisymmetrised wave functions, the evaluation of

where $f_k^r(f, d)$ and $g_k^r(f, d)$ are the angular parts of the ME's and $F_k(4f, 5d)$ or simply $F_k(f, d)$ and $G_k(4f, 5d)$ or simply $G_k(f, d)$ are the radial parts known as the Slater integrals, and these have been defined by Condon and Shortley [17].

$$\langle \Psi | H_{el}(f, d) | \Psi \rangle = \sum_{k=0}^{\infty} [f_k^r(f, d)F_k(4f, 5d) + g_k^r(f, d)G_k(4f, 5d)] \quad \dots(2)$$

$H_{el}(f, d)$ between the set is of the form [15, 16] – symmetrised wavefunctions of the mixed configuration $4f^k 5d$, then the ME's of ME's when acting between anti – symmetrised wavefunctions. If Ψ is a set of anti that $H_{el}(f, d)$ being a two - particle operator yields the direct and exchange direct Coulomb and exchange interaction components. This derives from the fact The electrostatic interaction operator $H_{el}(f, d)$ can be partitioned into the configuration have been completely evaluated and tabulated [14].

ME's of these operators between SL – coupled wavefunction of the $4f^k$ act on the electron states of the $4f^k$ configuration. In fact, the matrix elements has been expressed in terms of suitable generalized tensor operator [13] which between the $4f^k$ are electrons and the lone $5d$ electron. The operator $H_{el}(f, d)$ represents the electrostatic interactions between pairs of electrons in the $4f^k$ sub – configuration and $H_{el}(f, d)$ represents the interaction where $H_{el}(f, d)$ represents the electrostatic interactions between pairs of

$$H_{el} = H_{el}(f, d) + H_{el}(f, d) \quad \dots(1)$$

$4f^k 5d$ electrons can be written as The electrostatic interactions, which perturb the zero – order wave function of the

2. THEORETICAL FORMULATION

2.1 Electrostatic Perturbation Hamiltonian

configuration shall be computed and presented. $V_{el}^{(k)}$, $k = 0, 1, 2, \dots, 6$, between SL – coupled wave functions of the $4f^k$ In this paper, the general procedure for calculating the matrices of $H_{el}(f, d)$ in the Yanase Kasuya coupling formalism will be outlined. In particular the RME's of of the ions in potassium and rubidium halide crystals. [10] obtain a satisfactory fit between the theoretical energy levels of Sm^{2+} ions in octahedral environment and the experimentally observed individual energy levels components of $H_{el}(f, d)$ interactions when applying the Yanase – Kasuya coupling scheme to the $4f^k(FH)5d$ sub – configuration of Sm^{2+} ions, Mejeha and Smith assuming the partial cancellation of the Coulomb and the anisotropic exchange estimates of the $4f^k(FH) 5d$ sub – configuration [7]. Nevertheless without

And

$$Og^k(f,d) = D_k OG_k'(f,d) \dots (6b)$$

are the effective interaction operators that act on the angular component of the systems wavefunction, D_k being the denominators defined by Condon and Shortley [17] for the fd configuration. In particular

$$Of^{(2)}(f,d) = 70\sqrt{6U_f^{(2)} \cdot u_d^{(2)}}$$

$$Of^{(4)}(f,d) = 126\sqrt{55U_f^{(4)} \cdot u_d^{(4)}}$$

and

$$Og^k(f,d) = -\frac{1}{2} D_k \sum_{r=0}^4 [Y_r U_f^{(r)} \cdot u_d^{(r)} + Z_r V_f^{(1r)} V_d^{(1r)}] \dots (8)$$

where Y_r and Z_r are coefficients. The ME's of $Of^k(f,d)$ and $Og^k(f,d)$ between appropriate wavefunctions give the coefficients $f^k(f,d)$ and $g^k(f,d)$ respective of $F_k(f,d)$ and $G_k(f,d)$ in the energy matrices. Eqn. (2) can now be written as

$$\langle \Psi | H_{el}(f,d) | \Psi \rangle = \sum_{k=0}^{\infty} [f^k(f,d)F_k(4f,5d) + g^k(f,d)G_k(4f,5d)]$$

2.2 Basic Functions

In the Yanase -Kasuya coupling scheme, a general representation of the basic functions of the low - lying states of the $4f^n 5d$ configuration is given as [9]

$$|f^n[\tau_1(S_1S)S_2L_1] J_2, \Gamma_d; \alpha_2 \Gamma \gamma \rangle \dots (10)$$

where τ_1 is an index which represents a set of quantum numbers needed to uniquely distinguish between coupled states of the $4f^n$ core electron with the same SL - values. Usually the set consists of irreducible representations of the continuous group R_7 and its sub - group G_2 [11,17,18]. Γ_d are quantum numbers used to represent the orbital states of the 5d electron. They are irreducible representatives of the point symmetry group, G, of the site of the impurity ions according to which the states of 5d electron transform. The quantum numbers, Γ are the irreducible representations of G which are spanned by the coupled basis functions of the mixed configuration while the index α_2 distinguishes between Γ 's of the same type and the same J - values and γ identifies the row of Γ to which the basis function belongs

In the octahedral crystal field, $\Gamma_d = \Gamma_3, \Gamma_5$ which are respectively the two and three dimensional irreducible representations of O_h point group. The states spanning Γ_3 and Γ_5 couple with the core electron states to yield the crystal field states denoted by the irreducible representations Γ_i ($i = 1, 2, \dots, 5$) or O_h point group as quantum numbers. Group theory predicts that the 140 free ion energy levels of the $4f^5(\text{PFH})5d$ sub – configuration of Sm^{2+} ions will be split into 525 crystal field levels. These levels are associated with crystal wave functions, which transform according to the irreducible representations of the O_h point group as follows:

$$50\Gamma_{1u} \oplus 55\Gamma_{2u} \oplus 105\Gamma_{3u} \oplus 155\Gamma_{4u} \oplus 160\Gamma_{5u} \dots (11)$$

The subscript u shows that the functions are of odd parity

The assumption that only electric dipole transitions of the impurity Sm^{2+} ions are permissible requires that electronic transitions from the ${}^7F_0(\Gamma_{1g})$ ground state terminate only at the $155\Gamma_{4u}$ levels during an optical excitation of the ions. As a result, only optical absorption bands ascribable to transitions to the $155\Gamma_{4u}$ levels of the $4f^5(\text{PFH}) 5d$ sub-configuration of Sm^{2+} ions in octahedral crystal field are expected to be observed. This reduces the size of the energy matrices to be computed during any study aimed at analyzing and interpreting the experimental spectra from 525 to 155.

2.3 Matrix Element of $H_{el}(f,d)$ in the Yanase –Kasuya Coupling Scheme.

The calculation of the matrix elements, ME's of $H_{el}(f,d)$ between the basis function (10) revolves around taking the ME's of the scalar products of the type $U_f^{(r)} \cdot u_d^{(r)}$ and $V_f^{(1r)} \cdot v_d^{(1r)}$ between those basis function. This requires recoupling of the angular momenta. Following Asano [9] we write:

$$\begin{aligned} & \langle f^{th} [\tau_1(S_1S_3)S_2L_1]J_2, \Gamma_d; \alpha_2\Gamma_\gamma | U_f^{(r)} \cdot u_d^{(r)} | f^n [\tau_3(S_3S_5)S_4L_3]J_4, \Gamma_d; \alpha_4\Gamma_\gamma \rangle \\ & = \delta(S_1, S_3)\delta(S_2, S_4)(-1)^{S_2+L_3+J_2+r} [J_2, J_4]^{1/2} \begin{Bmatrix} S_2 & L_1 & J_2 \\ r & J_4 & L_3 \end{Bmatrix} \\ & X \langle f^n \tau_1 S_1 L_1 | | U_f^{(r)} | | f^n \tau_3 S_3 L_3 \rangle W[d(\Gamma_d)J_d, d(\Gamma_d')J_4, \alpha_2\alpha_4\Gamma_\gamma] \dots (12) \end{aligned}$$

where on the right hand side of the equation, the symbol $[a, b, \dots] = (2a+1)(2b+1) \dots$, the second to the last factor is the reduced matrix element, RME, of $U_f^{(r)}$ between SL – coupled wrefunctions of the $4f^n$ configuration. They are given as [15]

$$\langle f^n \tau_1 S_1 L_1 | | U_f^{(r)} | | f^n \tau_3 S_3 L_3 \rangle$$

$$= n [L_1, L_3]^{1/2} \sum_{\bar{r} \bar{S} \bar{L}} \left\langle f^n \tau_1 S_1 L_1 \left\{ \left\langle f^{n-1} \bar{r} \bar{S} \bar{L} \right\rangle \left\langle f^{n-1} \bar{r} \bar{S} \bar{L} \right\rangle \right\} f^n \tau_3 S_3 L_3 \right\rangle$$

$$\times (-1)^{\bar{L} + L_1 + 3 + r} \begin{Bmatrix} L_1 & 3 & \bar{L} \\ 3 & L_3 & r \end{Bmatrix} \dots (13)$$

where on the right - hand side of Eqn (13), the first two factors under the summation sign are the coefficient of fractional parentage introduced by Racah [10 , 11] in order to antisymmetrise coupled wavefunctions of electrons in a configuration of many equivalent electrons. They have been calculated and tabulated for the f^n configurations [14].

The last factor in Eqn (12) are block coefficients which are analogous to those introduced by Asano [9]. The are given as

$$W[d(\Gamma_d) J_2, d(\Gamma'_d) J_4, \alpha_2 \alpha_4 \Gamma r] = \sum (q M_2 M_4 m_d m'_d) (-1)^{J_2 - M_2 + 2 - m_d}$$

$$\times A_2 \left[J_2 M_2 \left(\begin{smallmatrix} \beta \\ 2 \end{smallmatrix} \Gamma_{J_2} \right), dm_d (\Gamma_d)^{\alpha_2} \Gamma \gamma \right] A_4 \left[J_4 M_4 \left(\begin{smallmatrix} \beta \\ 4 \end{smallmatrix} \Gamma_{J_4} \right), dm'_d (\Gamma'_d)^{\alpha_4} \Gamma \gamma \right]$$

$$\times \begin{pmatrix} J_2 & r & J_4 \\ -M_2 & q & M_4 \end{pmatrix} \begin{pmatrix} 2 & r & 2 \\ -m_d & q & m'_d \end{pmatrix} \dots (14)$$

where we have enclosed the summation indices in a bracket in front of the summation sign for convenience. The block coefficient A_2 are defined as

$$A \left[JM \left(\begin{smallmatrix} \beta \\ J \end{smallmatrix} \Gamma_J \right), dm_d (\Gamma_d), \alpha \Gamma_\gamma \right] = \sum_{\gamma_J \gamma_d} \left\langle JM \left| \begin{smallmatrix} \beta \\ J \end{smallmatrix} \Gamma_J \gamma_J \right. \left. \left(dm_d \Gamma_J \gamma_J \Gamma_d \gamma_d \right) \right| \alpha \Gamma_\gamma \right\rangle$$

where $\langle JM, \begin{smallmatrix} \beta \\ J \end{smallmatrix} \Gamma_J \gamma_j \rangle$ and $\langle dm_d | \Gamma_d \gamma_d \rangle$ are symmetrized coefficients consistent with the transformation of the basis function into symmetry - adapted functions or lattice harmonic [19 - 23] while $\langle \Gamma_J \gamma_J \Gamma_d \gamma_d | \alpha \Gamma_\gamma \rangle$ are vector coupling or C.G. coefficients for crystal wave functions [23,24].

The ME's of the scalar product $V_f^{(ir)} \cdot v_d^{(ir)}$ between the basis functions (10) can be written as [9]:

$$\langle f^n [\tau_1 (S_1 S) S_2 L_1] J_2, \Gamma_d, \alpha_2 \Gamma_\gamma \left| V_f^{(ir)} \cdot v_d^{(ir)} \right| f^n [\tau_3 (S_3 S) S_4 L_3] J_4, \Gamma_d, \alpha_4 \Gamma_\gamma \rangle$$

$$= \delta (S_2, S_4) [J_2, J_4]^{1/2} (s(s+1)(2s+1))^{1/2} (-1)^{L_3 + S_3 + s + J_2}$$

$$\begin{aligned}
 & \times \left\{ \begin{matrix} S_1 & S_3 & 1 \\ s & s & S_2 \end{matrix} \right\} \left\{ \begin{matrix} L_1 & L_3 & r \\ J_4 & J_2 & S_2 \end{matrix} \right\} \langle f^n \tau_1 S_1 L_1 \| V_f^{1r} \| f^n \tau_3 S_3 L_3 \rangle \\
 & \times W \left[d(\Gamma_d) J_2, d(\Gamma'_d) J_4, \alpha_2 \alpha_4 \Gamma_r \right] \quad \dots (16)
 \end{aligned}$$

where the second to the last factor on the right - hand side of Eqn. (16) is the RME of $V_f^{(1r)}$ between SL -coupled wavefunctions of $4f^n$ electrons and is given as [15]

$$\begin{aligned}
 & \langle f^n \tau_1 S_1 L_1 \| V_f^{(1r)} \| f^n \tau_3 S_3 L_3 \rangle = n [s(s+1)(2s+1) [S_1, L_1, S_3, L_3]]^{1/2} \\
 & \times \sum_{\bar{r} \bar{S} \bar{L}} \langle f^n \tau_1 S_1 L_1 \left\{ \begin{matrix} f^{n-1} \bar{r} \bar{S} \bar{L} \\ \bar{r} \bar{S} \bar{L} \end{matrix} \right\} \langle f^{n-1} \bar{r} \bar{S} \bar{L} \rangle \rangle f^n \tau_3 S_3 L_3 \rangle \\
 & \times \left\{ \begin{matrix} S_1 & S_3 & 1 \\ s & s & \bar{S} \end{matrix} \right\} \left\{ \begin{matrix} L_1 & L_3 & r \\ 3 & 3 & \bar{L} \end{matrix} \right\} (-1)^{\bar{S} + \bar{L} + S_1 + L_1 + 3 + s + 1 + r} \quad \dots (17)
 \end{aligned}$$

The RME's of $V^{(11)}$ for f^n configuration have been tabulated by Nielson and Koster. Cowan [16] has reported that Karaziya and his associates have computed and tabulated the RME's $V^{(1r)}$, $r = 0, 1, 2, \dots, 6$ for f^n configurations up to $n = 4$. As far as the author knows tables of values of the RME's of $V^{(1r)}$ ($r = 0, 2, 3, \dots, 6$) for f^n , $n = 5, 6, 7$ have not been published and therefore not easily accessible if they exist.

3. RESULTS AND DISCUSSION

The matrix elements of the $H_{el}(f, f)$ interaction operator between the states of the $4f^6$ configuration were obtained from Nielson and Koster [14]. The term energies are

$$\begin{aligned}
 E[{}^6P] &= 10E^0 + 33E^3 \\
 E[{}^6F] &= 10E^0 \\
 E[{}^6H] &= 10E^0 + 9E^3
 \end{aligned}$$

Where E^i ($i = 0, 1, 2, 3$) are linear combinations of Slater - Condon integrals $F_k(f, f)$, $k = 0, 2, 4, 6$. [15]. The quantity $10E^0$, which is common to all term energies, was dropped since it does not affect the electronic energy structure of the configuration. Using the inter - conversion expression of term energies [15], we obtain:

$$\begin{aligned}
 E[{}^6P] &= 55F_2(f, f) + 66F_4(f, f) - 100F_6(f, f) \\
 E[{}^6P] &= 0
 \end{aligned}$$

$$E[{}^6\text{H}] = - 15F_2(f,f) - 18F_4(f,f) + 273F_6(f,f)$$

Values of $F_k(f,f)$, $K = 2,4,6$ were taken as those of $4f^5$ configuration of free Sm^{3+} ion [15].

For the computation of the energy matrices of $H_{el}(f,d)$, use was made of the various expressions developed in section two. The ME's of the operators $O_{f_k}(f,d)$ were computed by using Eqns. (7a,b), (12) and (13). Values of the RM's in Eqn (12) as well as the coefficients of fractional parentage for the f^5 configuration were obtained from Nelson and Koster [14] and the RME's cross - checked with eqn. (13). Values of the block coefficients $W []$ were computed in integer arithmetic and stored in a computer. The symmetrised coefficients

$\langle JM | \beta \Gamma_j \gamma_j \rangle$ and $\langle dm | \Gamma_d \gamma_d \rangle$ were obtained from Leushin [21] while the vector

coupling coefficients $\langle \Gamma_i \gamma_i \Gamma_j \gamma_j | \frac{1}{2} \Gamma_4 \gamma \rangle$, $i,j = 1,2,\dots, 5$ were obtained from Griffith

[23]. The $3-j$ and $6-j$ symbols were calculated in integer arithmetic by using a library of computer subroutines. In all, several tables of $W []$ were obtained.

They cannot be presented here because of their bulk. The computation of the $W []$ coefficients are very sensitive to errors in phase, particularly as the computation was carried out in integer arithmetic. That the computer programme worked through without hitches and error signals inspires confidence in the procedures adopted. The computed values were found to satisfy relevant orthogonality and symmetry relations [9] including

$$\sum_{J_2 \alpha_d \Gamma_d} (2J_2 + 1) w [d(\Gamma_d) J_2, d(\Gamma'_d) J_4, \alpha_2 \alpha_4 \Gamma_r] w [d(\Gamma_d) J_2, d(\Gamma'_d) J_4 \alpha_2 \alpha_4 \Gamma_r] \\ = (2r + 1)^{5/5} \delta(\alpha_2 \Gamma'_d, \alpha_4 \Gamma'_d); (|J_4 - r| \leq J_2 \leq J_4 + r) \quad \dots (18)$$

and

$$w [d(\Gamma'_d) J_4, d(\Gamma'_d) J_2, \alpha_4 \alpha_2 \Gamma_r] = (-1)^{J_4 - J_2} w [d(\Gamma_d) J_2, d(\Gamma'_d) J_4 \alpha_2 \alpha_4 \Gamma_r] \quad \dots (19)$$

With this procedure, values were obtained for $f_{(f,d)}^k$ which are the coefficient of $F_k(f,d)$, ($k = 2,4$) in Eqn. (9). $F_0(f,d)$ was dropped in the computation because it does not affect the structure of the electronic energy levels of the $4f^5 5d$ configuration.

As for the ME's of the $O_{f_k}(f,d)$ operators, the RME's of the operators $V_f^{(1r)}$, ($r = 0, 1, 2, \dots, 6$) between SL - coupled wave functions of the $4f^5({}^6\text{PFH})$ sub - configuration had to be calculated by using Eqn (19). They are presented in table 1. The ME's of the scalar products $U_d^{(r)} \cdot u_d^{(r)}$ and $V_f^{(1r)} \cdot v_d^{(1r)}$ were subsequently computed in integer arithmetic using a library of computer subroutines.

TABLE 1: Reduced matrix elements $\langle \tau_1 S_1 L_1 \parallel V^{(lr)} \parallel \tau_3 S_3 L_3 \rangle r=0, 1, \dots, 6$ for $4f^5$ (${}^6\text{PFH}$) sub-configuration. Only elements in the upper triangle of the matrix are given. Reflected elements in the lower triangle have the same values as those in the upper triangle.

r		$V^{(0)}$	$V^{(1)}$	$V^{(2)}$	$V^{(3)}$	$V^{(4)}$	$V^{(5)}$	$V^{(6)}$
L_1	6S_3L_3							
	6P	$\frac{3}{2}\sqrt{10}$	$\frac{1}{10}\sqrt{15}$	$\frac{3}{10}\sqrt{15}$	0	0	0	0
	6F	0	0	$\frac{729}{70}\sqrt{5}$	$\frac{3}{10}\sqrt{10}$	$\frac{1}{10}\sqrt{110}$	0	0
	6H	0	0	0	0	$-\frac{9}{7}$	$\frac{3}{2}$	$\frac{3}{10}\sqrt{5}$
	6F	$\frac{1}{2}\sqrt{210}$	$\frac{1}{10}\sqrt{210}$	$\frac{1}{30}\sqrt{210}$	$-\frac{1}{10}\sqrt{210}$	$\frac{1}{30}\sqrt{210}$	$\frac{1}{10}\sqrt{210}$	$\frac{1}{30}\sqrt{210}$
	6H	0	0	$-\frac{1}{15}\sqrt{330}$	$\frac{1}{10}\sqrt{330}$	$-\frac{32}{77}\sqrt{78}$	$\frac{2}{11}\sqrt{78}$	$\frac{13}{15}\sqrt{15}$
	6H	$\frac{1}{2}\sqrt{330}$	$\frac{1}{2}\sqrt{33}$	$\frac{1}{30}\sqrt{2145}$	0	$\frac{1}{15}\sqrt{390}$	$-\frac{1}{10}\sqrt{390}$	$\frac{53}{1155}\sqrt{102}$

Denoting by Q_r the ME's of $U_f^{(r)} \cdot u_d^{(r)}$ between the basis functions (10) and by Q_{1r} , those of $V_f^{(lr)} \cdot v_d^{(lr)}$ and using Eqn (8) the coefficients, $g^k(f,d)$ of $G_k(f,d)$, ($k = 1, 3, 5$) in the $H_{cl}(f,d)$ matrix can be written as

$$g^k(f,d) = -\frac{1}{2} \sum_{r=0}^4 [Y_{kr} Q_r + Z_{kr} Q_{1r}] \quad \dots (12)$$

Where the coefficients $Y_{kr} = D_k Y_r$ and $Z_{kr} = D_k Z_r$ are given in Table 2. The last now in the table headed by the index m_r , gives the constant with which each element in the column in which it appears has to be multiplied to get the actual values of Y_{kr} and Z_{kr} . Each negative entry is preceded by a minus sign. Thus

$$Y_{53} = -77\sqrt{15} \text{ and } Z_{31} = 36\sqrt{70}$$

Eventually two energy matrices were composed one each for $H_{cl}(f,f)$ and $h_{el}(f,d)$ interactions. They were then summed to obtain the composite electrostatic

energy matrix for the sub configuration. Its elements were expressed in terms of the Slater – Condon parameters $F_k(f,f)$, $k = 2,4,6$ for $H_{el}(f,f)$ component and $G_k(f,d)$, ($k = 2,4$) and $G_k(f,d)$, $k = 1,3,5$, for $H_{el}(f,d)$ component. The matrices cannot be presented here because of their bulk.

Part of the composite energy matrix has been used by Mejeha and Smith [10] in their calculation of the electronic energy spectrum of the $4f^5(^6PFH)5d$ sub – configuration of Sm^{2+} ions in octahedral environment. In that study, they obtained a satisfactory fit between the energy levels of the first four groups of bands on the absorption spectra of Sm^{2+} ions in potassium and rubidium halide crystals and the calculated energy levels of that sub – configuration, after incorporating other important interaction matrices. They were also able to obtain optimized values of the energy parameters $F_2(f,d)$ and $G_1(f,d)$ for Sm^{2+} ions in those crystals. We anticipate an improved result if the entire energy matrices of the $4f^5(^6PFH)5d$ sub – configuration are used to fit all experimentally observed energy levels of Sm^{2+} ions.

TABLE 2: Values of the coefficient Y_{kr} and Z_{kr} appearing in Equation (20)

k	r	$Y_{kr}=D_k Y_r$				$Z_{kr}=D_k Z_r$				
		1	2	3	4	0	1	2	3	4
1		2	6	3	1	4	8	24	12	4
3		3	-11	-8	4	16	12	-44	-32	16
5		-33	55	-11	1	88	-132	220	-44	4
m_r		$3\sqrt{70}$	$5\sqrt{6}$	$7\sqrt{15}$	$9\sqrt{55}$	$3\sqrt{35}$	$3\sqrt{70}$	$5\sqrt{6}$	$7\sqrt{15}$	$9\sqrt{55}$

4.

SUMMARY

In this paper, we have discussed the procedures for calculating the electrostatic energy matrices for low – lying levels of the $4f^5(^6PFH)5d$ sub – configuration of Sm^{2+} ions in octahedral environment within the framework of the Yanase – Kasuya coupling formalism while employing the Racah irreducible tensor operators $V^{(r)}$, ($r = 0,2,\dots,6$) between SL – coupled wave – functions of the $4f^5(^6PFH)$ sub-configuration were calculated and presented. These are not easily accessible in literature. In addition, the $W []$ block coefficients introduced to take care of the influence of the crystalline environment on the free – ion wavefunctions were also computed. These enabled the elements of the $H_{el}(f,d)$ matrix to be obtained and expressed in terms of $F_k(f,d)$ and $G_k(f,d)$ which are regarded as adjustable energy parameters.

Although these results have not been previously published, they have been used in part in a scheme for calculating energy spectrum of the $4f^5(^6\text{PFH})5$ sub - configuration with satisfactory results.

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