

Spin correlation in Pr IV and Tm IV free ions

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Received: 17 October 2013 / Accepted: 25 April 2014 / Published online: 4 May 2014
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Abstract The coefficients c_k ($k = 2, 4, 6$) that pertain to spin-correlated matrix elements of the tensor operator $U^{(k)}$ have been evaluated by means of the differences $U^{(k)}$ (intermediate) – $U^{(k)}$ (LS) and the reduced matrix elements of the operator $V^{(Ik)}$. Only spin-allowed transitions have been considered from each ground level to the excited energy levels within the $4f^2$ and $4f^{12}$ configurations of the free ions Pr (3+) and Tm (3+), respectively. The values of the coefficients c_k thus found correspond in most cases by sign and order of magnitude to those determined in other sources as corrections to lanthanide (3+) crystal-field parameters.

Keywords Spin correlation · Free ions · Praseodymium (3+) · Thulium (3+)

Mathematics Subject Classification 81V45

1 Introduction

The problem of spin correlation has been raised by Newman in order to explain the crystal-field (CF) splitting of the ground level $^8S_{7/2}$ in Gd^{3+} [1]. Judd has proposed general formulae for its evaluation and discussed several examples of the spin-correlation effect on the CF parameters of Ln^{3+} [2, 3]. Later, various research groups have contributed to the solution of the problem either in theoretical plan or with semi-empirical estimates of this effect.

The mechanism of spin correlation is based on the energy difference of the open-shell electrons originating from different spin orientation. The electrons with parallel spins have lower net repulsion due to attractive exchange and direct Coulomb inter-

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actions resulting in more compact radial distribution and increased Slater parameters compared to the electrons with antiparallel spins [4,5].

Positive contributions to the coefficients c_k have been found to arise from 4f–3p covalency in $\text{Eu}^{3+} - \text{Cl}^-$ [4]. Significant corrections to the Slater parameters $F^{(k)}$ for Pr^{3+} have been obtained by considering spin-correlated Coulomb interaction and found of equal importance compared with other contributions [5]. The effect of spin correlation on the conventional CF parameters $A_k^q < r^k >$ has been calculated for the system $\text{Gd}^{3+} - \text{Cl}^-$ by means of the coefficients c_k [6]. It has been shown that the spin-correlated CF operator is diagonal in the total spin S of an open shell [7]. The spin correlation has been included as separate contribution to the splitting of the $^8S_{7/2}$ of Gd^{3+} [8].

The energy levels of $\text{Gd}^{3+} : \text{LaCl}_3$ and $\text{Ho}^{3+} : \text{LaCl}_3$ have been fitted with 12- and 20-parameters respectively and the upper bounds of the spin-correlation coefficients c_k estimated [9]. The same coefficients have been determined for eight Ln^{3+} ions ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Pm}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}$) by fitting the available energy levels of these ions in LaCl_3 matrix [10]. A sixth-rank spin-correlated crystal-field operator has been found useful in the interpretation of the structure of the $^2\text{H}(2)_{11/2}$ multiplet of Nd^{3+} in several host crystals [11].

A more recent study deals with spin-correlated CF analysis of Ln^{3+} ($\text{Ln} = \text{Sm}, \text{Eu}$ or Tb) in cubic sites of elpasolites, $\text{Cs}_2\text{NaLnX}_6$ [12].

Almost all features of the spin correlation have been examined so far mostly on the system $\text{Ln}^{3+} : \text{LaCl}_3$. In addition, the estimates of the spin-correlation effect have been obtained only as corrections to CF parameters. The present report is aimed at the evaluation of the spin-correlation coefficients c_k ($k = 2, 4, 6$) of the free ions Pr IV and Tm IV for their triplet energy levels above each triplet ground level.

2 Method

The values of the coefficients c_k ($k = 2, 4, 6$) have been calculated according to the following formula modified from that one used by various authors [2,4,7]:

$$c_k = \frac{\langle \psi \| U^{(k)} \| \psi' \rangle_{IM} - \langle \psi \| U^{(k)} \| \psi' \rangle_{LS}}{[S(S+1)/(2S+1)]^{1/2} \langle \psi \| V^{(1k)} \| \psi' \rangle}, \quad (1)$$

where the reduced matrix elements of the tensor operator $U^{(k)}$ are between wave functions in intermediate (IM) and LS bases, S is the total spin quantum number of the energy level $^{2S+1}L_J$, and $\langle \psi \| V^{(1k)} \| \psi' \rangle$ are the reduced matrix elements of the tensor operator $V^{(k)}$ between the wave functions ψ and ψ' . The above expression applies only to wave functions with the same spin, $S = S'$, $\delta(S, S') = 1$, i.e. the delta function is implicitly included in Eq. 1 [7]. It is assumed in the present study that the reduced matrix elements between wave functions in IM basis $\langle \psi \| U^{(k)} \| \psi' \rangle_{IM}$ contain correction factors proportional to c_k .

The matrix elements of the tensor operator $U^{(k)}$ have been determined as products of 6j-symbols and doubly reduced matrix elements of the configurations $4f^2$ and $4f^{12}$ by the expression given below:

$$\begin{aligned}
 & \left\langle f^N \alpha L S J \left\| U^{(k)} \right\| f^N \alpha' L' S' J' \right\rangle \\
 &= (-1)^{S+L'+J+k} \delta(S, S') \left[(2J+1)(2J'+1) \right]^{1/2} \\
 & \quad \times \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \left\langle f^N \alpha L S \left\| U^{(k)} \right\| f^N \alpha' L' S' \right\rangle
 \end{aligned} \quad (2)$$

The wave functions in IM basis of the free ions Pr IV and Tm IV have been reported previously [13]. Since the open subshell $4f^{12}$ (Tm IV) is complementary to the closed subshell $4f^{14}$ by the open subshell $4f^2$ (Pr IV), the following relationship holds between the corresponding matrix elements [14]:

$$\begin{aligned}
 & \left\langle f^{14-N} \nu L S \left\| Q^{(qk)} \right\| f^{14-N} \nu' L' S' \right\rangle \\
 &= -(-1)^{[(\nu-\nu')/2]+q+k} \left\langle f^N \nu L S \left\| Q^{(qk)} \right\| f^N \nu' L' S' \right\rangle
 \end{aligned} \quad (3)$$

where ν and ν' designate seniority numbers; with $Q = U$, $q = 0$, and with $Q = V$, $q = 1$.

A transponding relationship between the reduced matrix elements has been applied in order to select the appropriate sequence of the energy levels for each transition:

$$\left\langle f^N \alpha L S \left\| Q^{(qk)} \right\| f^N \alpha' L' S' \right\rangle = (-1)^{L+S-L'-S'} \left\langle f^N \alpha' L' S' \left\| Q^{(qk)} \right\| f^N \alpha L S \right\rangle \quad (4)$$

where $Q = U$ or V are the same as above, α and α' are unspecified quantum numbers.

The doubly reduced matrix elements $\| U^{(k)} \|$ and $\| V^{(k1)} \|$ are available for all pairs of multiplets of f^2 [14]. The 6j-symbols have been determined after the procedure prescribed by Jucys and Bandzaitis [15].

Table 1 Matrix elements of the tensor operator $U^{(k)}$ in IM and LS couplings and spin-correlation coefficients c_k for spin-allowed transitions of Pr IV

${}^3H_4 \rightarrow$	3H_5	3H_6	3F_2	3F_3	3F_4	3P_0	3P_1	3P_2
$U_{IM}^{(2)}$	0.5730	0.0258	1.2189	0.4445	0.2084	0	0.0252	0.0057
$U_{IM}^{(4)}$	-0.7818	-0.3009	1.1002	1.0229	0.3291	0.7090	0.7308	0.3080
$U_{IM}^{(6)}$	-1.3523	-0.7232	-0.6067	-1.4490	-1.1334	0	0	-0.6564
$U_{LS}^{(2)}$	0.5674	0.0750	1.2234	0.4577	0.0904	0	0	0
$U_{LS}^{(4)}$	-0.8218	-0.2478	1.1199	1.0476	0.4253	0.6901	0.7559	0.3481
$U_{LS}^{(6)}$	-1.3234	-0.6843	-0.6513	-1.4564	-1.1282	0	0	-0.7252
c_2	0.0053	-0.0469	-0.0054	-0.0158	0.1410	0	0	0
c_4	0.0440	0.0584	-0.0194	-0.0243	-0.0947	0	-0.0364	-0.0581
c_6	0.0249	0.0335	-0.0358	-0.0059	0.0042	0	0	-0.1486

Table 2 Matrix elements of the tensor operator $U^{(k)}$ in IM and LS couplings and spin-correlation coefficients c_k for spin-allowed transitions of Tm IV^(a)

${}^3H_4 \rightarrow$	3F_4	3H_5	3H_4	3F_3	3F_2	3P_0	3P_1	3P_2
$U_{IM}^{(2)}$	1.2214	0.5675	0.9130	1.4653	0	0	0	0
$U_{IM}^{(4)}$	1.4075	0.8331	0.6722	0.9741	0.4593	0.7264	1.1202	1.0170
$U_{IM}^{(6)}$	0.8362	1.3837	1.3447	1.5883	0.8546	0.4649	0.6096	0.1245
$U_{LS}^{(2)}$	1.5736	0.5701	0.0748	1.4720	0	0	0	0
$U_{LS}^{(4)}$	1.6242	0.8368	0.2478	0.9785	0.2500	0.7502	1.1252	1.2993
$U_{LS}^{(6)}$	1.4355	1.3899	0.6843	1.5955	0.9535	0.4629	0.6124	0.4129
c_2	0.4214	0.0024	-0.7866	0.0080	0	0	0	0
c_4	0.2133	-0.0042	0.4671	0.0043	-0.2061	0.0345	0.0074	0.4094
c_6	-0.4805	-0.0054	0.5685	-0.0057	-0.0793	0.0043	-0.0060	1.1611

(a) The non-zero values of $\|U^{(k)}\|$ are negative

Table 3 Coefficients c_k of spin-correlation for lanthanide ions

Level, Ln ³⁺ , matrix	c_2	c_4	c_6	Ref.
${}^6I_{17/2}$, Gd ³⁺ : LaCl ₃ ,	$\leq 0.05 $	$\leq 0.1 $	$\leq 0.3 $	
6P_J , Gd ³⁺ : LaCl ₃	-0.03			[2]
3K_8 , Ho ³⁺ : LaCl ₃			-9 (-0.01)	
Eu ³⁺ - Cl ⁻	-0.11 ± 0.13	-0.10 ± 0.15	-0.14 ± 0.15	[4]
${}^8S_{7/2}$, Gd ³⁺ - Cl ⁻	-0.149	-0.147	-0.141	[6]
${}^6I_{17/2}$, Gd ³⁺ : LaCl ₃ ,	$< 0.05 $	$< 0.1 $	$< 0.3 $	[9]
3K_8 , Ho ³⁺ : LaCl ₃				
LaCl ₃ : Pr ³⁺ ,	(0.021)	-0.085	(0.005)	
Nd ³⁺ ,	0.156	0.093	0.032	
Pm ³⁺ ,	(0.047)	-0.040	0.117	
Sm ³⁺ ,	(0.008)	(0.062)	0.060	[10] ^(b)
Gd ³⁺ ,	(-0.004)	-0.044	0.133	
Dy ³⁺ ,	(-0.027)	(0.022)	0.042	
Ho ³⁺ ,	0.038	-0.107	0.135	
Er ³⁺	0.120	-0.096	-0.305	
${}^8S_{7/2}$, Gd ³⁺ :	0.07			[16]
C ₂ H ₅ SO ₄ ·9H ₂ O				

(b) Values in parentheses reported ill-determined in both sign and magnitude

3 Results and discussion

Tables 1 and 2 contain coefficients c_k of spin correlation determined after Eq. 1 as well as the necessary matrix elements $\langle \psi \| U^{(k)} \| \psi' \rangle$ in two approximations whereas the available c_k 's needed for comparison are compiled in Table 3. If the coefficients

of spin correlation $c_k < 0$, slight contraction of the radial wave functions takes place, $c_k > 0$, respective expansion, and with $c_k = 0$, lack of change due to spin correlation. The zero values are due to zero reduced matrix elements of $U^{(k)}$ and $V^{(k)}$.

All triplet—triplet transitions ${}^3H_4 \rightarrow {}^3H_J, {}^3F_J, {}^3P_J$, of the free ion Pr IV are presented in Table 1. When the values of c_k 's from this table are compared with those known for $Pr^{3+} : LaCl_3$ and quoted in Table 3, it is seen that they have nearly the same magnitude in the range $(-0.15, 0.15)$ and about half of our coefficients c_k are negative. It has been shown that the sign of the coefficients c_k depend on the mechanism considered to get agreement with experimental zero field splittings and in particular, for Gd^{3+} in lanthanum ethylsulphate $c_k > 0$ [16]. It should be noted that the spin-correlation coefficients c_k in Table 1 have small, but specific values for each transition.

About 2/3 of the spin-correlation coefficients obtained in this work for Tm IV are compatible with those given in Table 3; some of the higher values of c_k in Table 2 are close to the values of c_k for neighboring Er^{3+} in Table 3. It has been noted that certain lower values of c_k in Table 3 have been determined by the authors with insufficient accuracy [10]. On the other side, values much higher than $c_6 \approx 1.2$ for Tm IV has been proposed, e.g. for the level 3K_8 of $Ho^{3+} : LaCl_3$, $c_6 = -9$ [2].

4 Conclusions

The spin-correlation effect studied in this work reveals the following features:

- (i) the coefficients c_k represent corrections to the matrix elements $\langle \psi \| U^{(k)} \| \psi' \rangle$ and are characteristic for each triplet level ${}^3H_J, {}^3F_J$, and 3P_J above the ground level 3H_4 (Pr IV) or 3H_6 (Tm IV). Most c_k 's determined here correspond by order of magnitude and sign to the reported overall c_k 's estimated from energy-level fitting procedures for $Ln^{3+} : LaCl_3$;
- (ii) it exerts small changes on the radial wave functions since $\| c_k \| \leq 0.15$ in more than 80% of the mentioned transitions;
- (iii) it can be determined for the free ions Ln IV apart from the spin-correlated crystal-field effect of trivalent lanthanides. The calculation is direct and based on the assumption that the corrected (or intrinsic) matrix elements $\langle \psi \| U^{(k)} \| \psi' \rangle$ are between wave functions in IM coupling approximation. These wave functions have been derived from experimental optical spectra of the mentioned free ions in the respective $4f^2$ and $4f^{12}$ configurations [13].

Acknowledgments The author would like to thank Prof. B. M. Angelov for pointing out the problem.

References

1. D.J. Newman, Chem. Phys. Lett. **6**(4), 288 (1970)
2. B.R. Judd, Phys. Rev. Lett. **39**(4), 242 (1977)
3. B.R. Judd, *Correlation Crystal Fields for Rare Earths and Actinides* (Int. Conf. on Luminescence, Paris, 1978)
4. D.J. Newman, G.G. Siu, W.Y.P. Fung, J. Phys. C Solid State Phys. **15**, 3113 (1982)
5. G.G. Siu, D.J. Newman, J. Phys. C Solid State Phys. **16**, 7019 (1983)

6. D.J. Newman, J. Phys. C Solid State Phys. **10**, L617–L620 (1977)
7. D.J. Newman, G.G. Siu, J. Phys. C Solid State Phys. **16**, L157–L158 (1983)
8. G.G. Siu, D.J. Newman, J. Phys. C Solid State Phys. **15**, 6753 (1982)
9. H. Crosswhite, D.J. Newman, J. Chem. Phys. **81**(11), 4959 (1984)
10. C.K. Jayasankar, F.S. Richardson, M.F. Reid, J. Less-Common Met. **148**, 289 (1989)
11. C.L. Li, M.F. Reid, Phys. Rev. B **42**, 1903 (1990)
12. J.R.G. Thorne, C.S. McCaw, R.G. Denning, Chem. Phys. Lett. **319**(334), 185 (2000)
13. D. Petrov, B. Angelov, J. Math. Chem. **51**, 2179 (2013)
14. R.I. Karaziya, YaI Vizbaraite, Z.B. Rudzikas, A.P. Jucys, *Tables for Calculation of Matrix-Element Operators of Atomic Quantities* (Academic Science, Moscow, 1972), p. 28
15. A.P. Jucys, A.A. Bandzaitis, *Theory of Angular Momentum in Quantum Mechanics* (Mokslas, Vilnius, 1977)
16. J.M. Dixon, R. Chatterjee, Phys. Status Solidi (b) **99**, 313 (1980)