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New analyses of energy level datasets for $LaCl_3:Ln^{3+}$ (Ln = Pr, Nd, Er)

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ABSTRACT

The electron spin-spin interaction (H_{ss}) has long been omitted by many previous researchers in the empirical study of lanthanide spectroscopic data in the last four decades. In this work, the corresponding operator is specifically included into the semi-empirical Hamiltonian for $4f^{N}$ tripositive lanthanide ions and its consequences are investigated by fitting the experimental energy level data available for LaCl₃ doped with Pr³⁺, Nd³⁺ and Er³⁺, taking into account polarization and Zeeman studies. The inclusion does not require additional parameters. For these systems, respectively: 61, 127, 83 experimental crystal field levels were fitted by 14, 20, 20 parameters, giving root mean square (r.m.s.) errors (in cm⁻¹) of 6.4, 8.1, 7.0. These errors are significantly smaller than those for best-fit calculations where H_{ss} is omitted. With the exception of calculations by Crosswhite et al. for Pr³⁺ and Nd³⁺, the results of our present fits are significantly different from those of many previous researchers, probably attributed to errors or improper use of the reduced matrix elements for various free-ion operators. The inclusion of H_{ss} into the energy level calculation can change state energies by almost three times the overall calculation r.m.s. error, and the changes vary considerably from one multiplet term to another. The spin-spin interaction has an effect upon the *I*-mixing between different multiplets and the impact can be appreciable in some cases, especially for dealing with the correlation crystal field. Since all the two body interaction operators are non-orthogonal within the $4f^{N}$ configuration, their corresponding free-ion parameters are correlated with each other, depending upon the set of energy levels chosen in the fit. Hence, there is much doubt about the reliability of parameter values as derived from previous studies which are quite different from those of our present study.

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1. Introduction

A major outcome from the electronic spectra of lanthanide ions (Ln^{3+}) is the assignment of the $4f^{N}$ energy levels. For the (gaseous) free ions, these are described under the Russell-Saunders scheme by the *J*-multiplets ${}^{2S+1}L_I$, where *S*, *L* and *J* denote the electron spin, orbital, and total (i.e. vector sum of *S* and *L*) angular momenta in units of h [1,2]. The mixing of different SL states, where S and/or L differ by one unit, with the same J manifold is determined by the spin–orbit coupling constant, ζ_f , so that the free ion energy levels of Ln³⁺ are described by intermediate coupling wavefunctions $[\alpha SL]$ with these combinations. At a crystalline site, the energy levels of these multiplets may be split into as many as 2J + 1 crystal field (CF) components for non-Kramers ions, depending upon the site symmetry of Ln³⁺, and these levels are identified by the irreducible representations (irreps) of the molecular site point group symmetry. In fact, wavefunctions of different *I*-multiplets can mix (i.e. *I*-mixing) when their irreps are the same, as determined by relevant CF parameters.

The calculation of energy levels of Ln^{3+} is made by fitting observed levels to a parameterized, semi-empirical Hamiltonian [3,4] by least-squares fitting diagonalization, since although *ab initio* methods have made recent progress [5–7], their accuracy is inferior. The Hamiltonian comprises "atomic" (i.e. spherically-symmetric) H_{AT}, and "crystal field, CF" H_{CF}, components:

$$\mathbf{H}_{\mathrm{AT}} = E_{AVE} + \sum_{k} F^{k} \mathbf{f}_{k} + \sum_{i} \zeta_{f} \mathbf{s}_{i} \cdot \mathbf{l}_{i} + H_{\mathrm{ADD}}$$
(1)

where:

$$\mathbf{H}_{\text{ADD}} = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{s} T^s \mathbf{t}_s + \sum_{k} P^k \mathbf{p}_k + \sum_{j} M^j \mathbf{m}_j$$
(2)

where k = 2, 4, 6; s = 2, 3, 4, 6, 7, 8; j = 0, 2, 4. The first term E_{AVE} (containing F^0 and the trace of other operators) adjusts the configuration barycenter energy with respect to other configurations. The Slater parameters F^k represent the electron–electron repulsion interactions and are two-electron radial integrals, where the f_k represent the angular operator part of the interaction. The Slater and spin–orbit coupling parameters are the most important in determining the atomic energies, as in Eq. (1). Certain additional parameters also affect the free ion energies, as shown in Eq. (2). The two-body configuration interaction parameters α , β , γ , parametrize the





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second-order Coulomb interactions with higher configurations of the same parity. For $4f^N$ and $4f^{14-N}$, N > 2 the three body parameters T^{s} are employed to represent Coulomb interactions with configurations that differ by only one electron from $4f^N$. With the inclusion of these parameters, the free ion energy levels can usually be fitted to within 100 cm⁻¹. The magnetic parameters M^{j} describe the spin-spin and spin-other orbit interactions between electrons, and the electrostatically correlated spin-orbit interaction P^k allows for the effect of additional configurations upon the spin-orbit interaction. Usually the ratios $M^0: M^2: M^4$ and those of $P^2: P^4: P^6$ are constrained to minimize the number of parameters, which otherwise already total 20. It is noted that in the present parametrization scheme, all those two-body interaction operators are not orthogonal to each other within the $4f^{N}$ -configuration, so their corresponding free-ion parameters (i.e. F^{k} , α , β , γ , P^{k} and M^{j}) are correlated with each other, and their fitted values will be dependent on the set of energy levels used in the fit. Furthermore, the threebody operator t_2 also contains some components of two-body interaction.

The H_{CF} operator represents the nonspherically symmetric components of the one-electron CF interactions, i.e. the perturbation of the $Ln^{3+} 4f^N$ electron system by all the other electrons in the crystal [3,4]. The states arising from the $4f^N$ configuration are wellshielded from the oscillating crystalline field (so that spectral lines are sharp) but a static field penetrates the ion and produces the Stark splitting of energy levels. The general form of the CF hamiltonian H_{CF} is given by:

$$H_{CF} = \sum_{i=1}^{N} \sum_{k=2,4,6} \sum_{q=-k}^{k} B_{q}^{k} \mathbf{C}_{q}^{k}(i)$$
(3)

where the B_q^k (hereafter B_{kq}) are the CF parameters and the $C_q^k(i)$ are tensor operators related to the spherical harmonics of rank k and component q; and the sum i is over all electrons of the $4f^N$ configuration. Some researchers also incorporate the two-electron CF (or the so-called correlation CF), like the spin-correlated CF (SCCF [8]), orbitally-correlated CF (LCCF [9]) and correlation CF with orthogonal operators (OCCF [10]), but they usually have very minor effects on the CF splittings except to rectify the calculated splittings in anomalous multiplets.

This type of energy level parametrization of Ln³⁺ energy levels in crystals has been widely employed for many decades, with various constraints of the parameters and inclusions of those in H_{ADD}. The major problems with these fitting methods concern both experiment and calculation. For the former, the incorrect assignment of energy levels to CF irreps introduces noise into the calculation, resulting in incorrect parameter values. Second, the insufficient characterization of a representative energy level dataset for a given 4f^N configuration produces biased parameter values, which only represent the multiplets sampled. Concerning the calculation itself, the presence of local minima may lead to incorrect parameter values. Frequently, for small datasets, only a small part of the relevant $4f^N$ configuration is included in the calculation; fixed parameter ratios are taken, or transferred/ extrapolated parameter values from other systems are employed, and this noise may be absorbed by other parameters and lead to spurious values. More fundamentally, there are errors not only in the fitting procedure, but in the matrix elements of the operators employed. Corrections to some of the matrix elements of the operators in H_{ADD} have previously been reported [11,12]. These parameters are generally envisaged to be of minor importance in fitting the energy levels of rare earth ions. However, in many cases the energy levels are assigned with reference to their ordering in the calculation so that levels which are fairly close in energy may be assigned to incorrect symmetry irreps. It is well-known that the energy level fitting of levels of certain multiplets, such as Nd³⁺ ²H(2)_{11/2}, and Pr³⁺ ¹G₄ (termed *rogue multiplets* by Denning [13]) normally results in inaccurate calculated energy values. In order to obtain more accurate fittings of these levels, refinements to theory have been made by inclusion of correlation effects between electrons [8–10,14–16], or inclusion of configuration interaction *via* the CF with other excited configurations [17,18].

Recently, Yeung [19] has found problems with the matrix elements connected with intra-atomic magnetic interactions in current use in computer programs and has provided new data tables for the matrix elements of spin–spin operators for $4f^N$ (N = 4-7). The problems arise due to the confusion of rank of the tensors which describe the spin–spin and spin–other orbit components of the Hamiltonian, as subsequently described. The relevant matrix elements are available in the literature for the $4f^2$ and $4f^3$ configurations only [20–22].

The purpose of the present study is to show the impact of these corrections upon $4f^{N}$ energy level calculations and to point out important cases where previous calculations have been in error. The incorporation of spin–spin interactions into the $4f^{N}$ energy level fittings now enables more accurate parameter values to be determined. The host lattice LaCl₃ doped with Ln³⁺ has been selected for illustration because, as pointed out by Morrison et al. [23], the optical spectra are the most extensively and accurately studied, and the site symmetry of Ln³⁺ is not low so that the number of parameters for energy level simulations is not excessive. Some reviews of parameter fits have previously been presented for these systems [23–27], but some more recent data are now available.

The crystal structure of LaCl₃ is depicted in Fig. 1. The C_{3h} site symmetry is preserved for Ln^{3+} doped at the La^{3+} site, although high resolution hyperfine studies show some symmetry lowering, due to random distortions [28]. Most prior calculations have utilized an assumed D_{3h} site symmetry to remove an imaginary CF parameter so that in Eq. (2) only 4 CF parameters are required [3]: B_{20} , B_{40} , B_{60} and B_{66} . This assumption is in fact unnecessary as the CF parameter B_{66} can be arbitrarily chosen to be real through a corresponding rotation of the coordinate frame around the *z*-axis. The Wybourne notation is employed herein. Most studies of LaCl₃:Ln³⁺ 4f^N systems have represented CF energy levels by crystal quantum numbers, μ [23], where for *N* even, $\mu = 0$, ± 1 , ± 2 , 3 and for *N* odd, $\mu = \pm 1/2$, $\pm 3/2$ and $\pm 5/2$. Herein, the states are also represented by irreducible representations (IRs) of C_{3h} .



Fig. 1. Coordination structure of LaCl₃ (data from Ref. [23]). The space group is *P*63/ *m* (No. 176), *Z* = 2. La³⁺ ions (large spheres) occupy C_{3h} sites, with Cl⁻ (small spheres) at C_s sites. The coordination polyhedron of La³⁺ is a tricapped trigonal pyramid with coordination number of 9.

2. Theory

The magnetic spin–spin interaction between the 4*f* electrons *i* and *j* with spins **s** is represented by the Hamiltonian H_{ss} [22,29]:

$$\mathbf{H}_{\rm ss} = 4\beta^2 \sum_{i>j} \left[\frac{\mathbf{s}_i \cdot \mathbf{s}_j}{r_{ij}^3} - \frac{3(\mathbf{r}_{ij} \cdot \mathbf{s}_i)(\mathbf{r}_{ij} \cdot \mathbf{s}_j)}{r_{ij}^5} \right] \tag{4}$$

where β is the Bohr magneton. The matrix elements of H_{ss} between multiplets ${}^{2S+1}L_{I}$ and ${}^{2S+1}L'_{I}$ are given by [22,29]:

$$<\gamma SLJ|\mathsf{H}_{ss}|\gamma'S'L'J'>=\delta(J,J')(-1)^{S'+L+J}\times\begin{cases}S'L'J\\L&S&2\end{cases}(\gamma SL||T^{(22)}||\gamma'S'L')$$
(5)

so that unless J = J' the element is zero. The 6 - j symbol gives further triangular inequality selection rules, e.g., $|S - 2| \leq S' \leq S + 2$ and $|L' - J| \leq S' \leq L' + J$, so that ΔS , $\Delta L = 0$, ± 1 , ± 2 [29]. From the first of these, it is noted that the matrix elements between singlet and triplet spin states, or between singlet spin states, are always zero. Notice that the tensor operator T is rank 2 in both spin and orbital space. In the Racah formalism, the states that enter into the relevant matrix elements are defined by the representations W and U of the respective groups R_7 and G_2 and further selection rules follow from group theoretical considerations [29]. The selection rules for spinspin interaction between different multiplets are less restrictive than those for spin-other orbit interaction, where the tensor operator is of rank one. Thus, when a spin-other orbit matrix element between the states may not be so.

The evaluation of the reduced matrix elements in Eq. (5) is carried out in terms of Marvin integrals [29], M^k . However, these integrals are also employed in parametrizing the spin–other orbit interactions, H_{soo}, where the corresponding tensor is of rank 1. Therefore the reduced matrix elements must be evaluated before the use of Eq. (5). This has not always been done in previous studies, and in fact most programs have neglected the inclusion of spin–spin interactions with the assumption that they are of minor importance. However, as will become apparent, this is not always the case. Therefore, as mentioned above, Yeung [19] has recently provided a tabulation of reduced matrix elements for spin–spin interaction for the configurations $4f^4-4f^7$ inclusive, which by symmetry also includes $4f^8-4f^{10}$.

This correction for spin–spin interaction does not introduce further parameters but leads to the inclusion of new matrix elements into the calculation. The spin–spin interaction is similar to, or sometimes greater than, the other magnetic interactions parametrized by M^k and P^k . If the spin–spin interaction is omitted from calculations when the other magnetic interactions are included, the resulting parameters, and the energy level fitting, will therefore not be accurate. Donlan [30] stated that he had calculated the spin–spin and spin–other-orbit matrices for the $4f^N$ configurations but his results were not published. However, we are unable to repeat the calculations of Donlan where spin–spin interactions were reportedly included, for CaF₂:Gd³⁺ [31], YAlO₃:Tm³⁺ [32], and YAlO₃:Er³⁺ [33].

Experimental energy level assignments have utilized polarization selection rules and Zeeman splittings. The first-order splitting, $s_{\alpha\mu}^{(1)}$ [34]:

$$\mathbf{S}_{\alpha\mu}^{(1)} = 2 < \alpha \mu | \mathbf{L}_z + 2\mathbf{S}_z | \alpha \mu >, \tag{6}$$

where the quantum numbers $\alpha \mu$ define the state, is zero for nondegenerate states. The correction to the above splitting, $s_{\alpha\mu}^{(2)}$, is obtained when the *J*-mixing generated by the magnetic field is included, to first order approximation, in the off-diagonal term [1,45]. The calculated values in Lorentz units are compared with the observed Zeeman splitting with the magnetic field along the *z* axis. For calculating the corresponding splitting s_x along the *x* axis, the relevant formulae from Section 6.6 in Wybourne's book [1] have been used. The computer program for the present fits and calculations was specifically developed by one of us and it had undergone rigorous comparisons with results given in some reliable sources (e.g. Refs. [1,4,11,17,18,21–23]).

3. Results and discussion

The effects of inclusion of spin-spin interaction in calculations of $LaCl_3:Ln^{3+}$ systems are exemplified through our calculations for the systems where Ln = Pr, Nd, Er, as follows.

3.1. $4f^2:Pr^{3+}$

The levels of LaCl₃:Pr³⁺ were determined by Sarup and Crozier [34] with the use of Zeeman studies, and some missing levels were subsequently filled in by Rana and Kaseta [35]. The levels are very close to those determined for PrCl₃ by Margolis [36], with the exception of the assignment of one of the ¹I₆ levels. The ¹S₀ level was determined later using two-photon spectroscopy [37]. The C_{3h} character table [36] and polarization selection rules for electric dipole transitions [34] have previously been given.

The parameter values are tabulated in Table 1 for the fit to all of the 61 levels of LaCl₃:Pr³⁺ with the r.m.s. error of 6.4 cm⁻¹ (with selected levels listed in Table 2, and the full Tables 2, 4 and 6 available in the Supplementary Data). The level ordering is correctly predicted, with the exception of the two close ${}^{3}F_{2}$ levels at 4950.4 (E') and 4958.3 (A'), whose separation is similar to the calculation error. Also, we have interchanged the irreducible representations (IRs) of levels 33 and 34 from previous tabulations on the basis of the Zeeman splitting [34] and the polarization in the absorption spectrum [35]. The parameter values for LaCl₃:Pr³⁺ from the fit of Crosswhite, who also included spin-spin interaction in his calculation [26], are also listed in Table 1. These parameters give an error of 210 cm⁻¹ for level 61, ¹S₀. Tröster et al. [38] fitted 29 levels from their high pressure data by constraining some parameter values in a calculation without spin-spin interaction. The resulting parameter values are also listed in Table 1, where B_{20} is ~10% higher than our value. However, it is noted that their fit to 61 levels at ambient pressure produced very similar parameter values to those in our present work. The levels exhibiting greatest discrepancy with calculation are from the singlets ${}^{1}D_{2}$ and ${}^{1}G_{4}$, and in this has been attributed previously to various interactions [9,17,18]. Garcia and Faucher [17,18] provided improved fits for these multiplets by including configuration interaction between $4f^2$ and $4f^{1}5d^{1}$. Only 43 levels were considered in their calculations. Note the typographical errors for ${}^{1}I_{6}$ and ${}^{3}P_{2}$ in their dataset (Ref. [18], Table 5). Their derived parameter values, notably for γ , differ from other studies (Table 1). Jayasankar and Richardson performed two calculations without the inclusion of spin-spin interaction [24], although their datasets were not shown. The first calculation employed 15 parameters, whereas the second included an additional 4 spin-correlated CF parameters (Ref. [24], Table 1). The improvement was not significant.

When our same parameter values as in Table 1 are employed in the calculation, but without spin–spin interaction, most levels decrease in energy by $1-2 \text{ cm}^{-1}$, but with some exceptions. The ${}^{3}\text{H}_{5}$ levels decrease by $\sim 5 \text{ cm}^{-1}$, ${}^{3}\text{P}_{0}$ increases by 20 cm^{-1} , and ${}^{3}\text{P}_{1}$ by 11 cm⁻¹ in the H_{ss} = 0 calculation. The three ${}^{3}\text{P}_{2}$ levels are at very similar energies (differences < 0.1 cm⁻¹) in the two calculations. To summarize, the energy shifts are much greater than the root mean square error of the calculation in some cases and the shifts vary considerably from one multiplet to another.

Table 1

²Parameters (cm⁻¹) for the calculations of $4f^2$ energy levels of Pr³⁺ in LaCl₃. N_p and N_{expt} are numbers of variable parameters and measured energy levels, respectively. For each parameter, the first column contains the best fitted values or fixed values used in the energy level calculation. The second column contains the uncertainties for the fitted parameters (square brackets mean the corresponding parameter is fixed rather than fitted).

Parameter	This work		Ref. [26]	Ref. [24]		Ref. [24] ^b		Ref. [38]		Ref. [18]
B ₂₀	106.3	1.1	107	108.3	5.9	106.1	5.9	118	7	96
B_{40}	-332.7	3.2	-342	-331.5	9.8	-344.8	10.6	-334	12	-348
B ₆₀	-651.8	2.1	-677	-652.9	11	-651.3	12.5	-668	17	-695
B ₆₆	447.0	1.8	466	444.7	8.6	464.2	10.2	442	11	465
ζ_f	748.0	0.3	744	749.3	2.8	749.3	2.8	746.3	4	750
F^2	68,439	7	68,368	68,443	9	68,443	9	68,399	16	69,741
F^4	50,226	23	50,008	50,186	17	50,186	17	50,173	40	53,620
F^6	32,973	23	32,743	32,973	12	32,973	12	32,909	35	36,901
α	22.8	0.1	22.9	22.84	0.94	22.84	0.94	[22.8]	1]	22.31
β	-676.0	3.6	-674	-682	8	-682	8	[-676	5]	-689.71
γ	1452.5	3.6	1520	1454	7	1454	7	[1453	5]	242.14
M^0	1.71	0.06	1.76	1.8	1.05	1.8	1.05	[1.72]	-
P^2	265.7	7.3	275	236	14	236	14	[266]	-
EAVE	9931.0	0.6	9928	9931	3	9931	3	9932	3	
σ	6.4			6.8		6.6		5.5		6.49 ^c
N_p	14			14		18		9		11
N _{expt}	61			61		61		29		43

^a The ratios $M^0:M^2:M^4$ and $P^2:P^4:P^6$ were fixed as 1.00:0.56:0.38 and 1.00:0.75:0.50, respectively in this work, as were values in square brackets. The r.m.s. error, σ_i is given by: $\sigma = \left[\sum_{i} \left(E_{obs}^{i} - E_{calc}^{i}\right)^{2} / N_{expt}\right]^{1/2}$, where N_{expt} is the number of levels fitted. b SCCF fit with b_{20} , b_{40} , b_{60} , b_{66} additional parameters.

^c Mean deviation.

Table 2 Observed (4.2 K [35,37]) and calculated energy levels for selected multiplets of Pr³⁺ doped into LaCl₃.^a

No.	SLJ	μ	C_{3h}	Eobs	Δ	s _{obs}	$ s^{(1)} _{calc}$	$ s^{(1)} + s^{(2)} _{calc}$
			irrep					
7	$^{3}H_{5}$	3	Α″	2137.2	5.8	0.00	0.00	0.00
8		2	E′	2169.8	7.1	0.0	0.11	0.14
9		1	E″	2188.5	-1.6	9.42	10.04	10.01
10		3′	Α″	2202.2	3.2	0.00	0.00	0.00
11		2′	E'	2222.6	-3.2		4.02	4.12
12		1'	E″	2266.9	9.5		1.80	1.83
13		0	A′	2283.8	-5.5		0.00	0.00
23	${}^{3}F_{2}$	1	E″	4922.6	-2.0	1.10	1.17	1.16
24		2	E'	4950.4	-0.3	2.69	2.72	2.73
25		0	A′	4958.3	12.8		0.00	0.00
33	${}^{3}F_{4}*$	0	A′	6772.1	4.1	0.0	0.00	0.00
34	*	2	E′	6781.9	13.2		2.55	2.53
43	$^{1}D_{2}$	0	A′	16630.5	-14.0	0.00	0.00	0.00
44		2	E′	16730.9	-11.3	3.76	4.14	4.14
45		1	E″	16780.5	24.6		2.07	2.07
46	³ P ₀	0	A′	20474.8	3.7	0.00	0.00	0.00
47	³ P ₁	1	E″	21066.4	-2.4	2.92	3.00	3.05
48		0	A′	21096.2	-5.2	0.00	0.00	0.00
49	${}^{1}I_{6}$	0	A′	21298.9	-0.6	0.00	0.00	0.00
50		0′	A′	21301.1	-3.4	0.00	0.00	0.00
58	${}^{3}P_{2}$	0	A′	22207.0	3.0	0	0.00	0.00
59		1	E″	22226.0	3.4	2.84	2.89	2.84
60		2	E′	22246.0	-1.8	5.80	5.81	5.81
61	${}^{1}S_{0}$	0	A′	46450.6	-0.3	0	0.00	0.00

^a μ is the crystal quantum number. E_{obs} are observed energies, given in cm⁻¹ units, Δ represents E_{obs} - E_{calc} where E_{calc} are calculated energies. The Zeeman splittings s_{obs} are from Ref. [34]. Asterisks (*) denote more than 10% mixing with another multiplet.

The ratios of $M^0: M^2: M^4$ in our fit in Table 1 were fixed at 1.00:0.56:0.31, and those of *P*²:*P*⁴:*P*⁶ at 1.00:0.50:0.10. Free variation of both parameters slightly improved the calculation error. but gave spurious negative parameter values for M^0 , M^2 and P^4 , in addition to unrealistic values of ζ_f (711 cm⁻¹) and β (-679.1 cm^{-1}) . The reason is that the matrices for the operators \mathbf{m}_0 and \mathbf{p}_4 are almost completely correlated and they are highly correlated with those of other affected parameters. Free variation of the M^k parameters, with P^k constrained to fixed ratios, gave the r.m.s. error of 6.1 cm^{-1} , with similar parameter values to those in Table 1, and the ratios of $M^0: M^2: M^4$ as 1.00:0.60:0.33, which are

Table 3 Energy parameters for Nd³⁺ in LaCl₃.^a

Ref. parameter	This wo	rk	Ref. [41]	Ref. [24]	Ref. [42]	Ref. [38]
B ₂₀	152.6	1.9	153	169.1	163	8	153	7
B ₄₀	-346.9	5.0	-344	-325.3	-336	22	-347	15
B ₆₀	-711.8	5.0	-724	-710	-173	22	-714	16
B ₆₆	468.3	2.8	474	457.2	462	17	468	13
F^2	71,934	18	71,890	71,872	71,866	42	71,922	22
F^4	52,276	35	52,230	52,283	52,132	77	52,259	37
F ⁶	35,466	29	35,486	35,554	35,473	41	35,488	44
ζ_f	879.1	0.3	879	879.1	880	1	874.9	1.0
M^0	1.942	0.021	1.84	1.83	1.97	0.10	1.92	0.09
P^2	281.0	4.1	281	256	255	23	288	20
α	22.14	0.03	22.118	22.13	22.08	0.10	22.16	0.08
β	-653.5	1.2	-656	-657	-650	5	-654	5
γ	1565.1	9.1	1583	1566	1586	12	1565	10
T^2	354.7	5.3	372	380	377	15	361	10
T^3	40.2	0.4	40	39	40	1	40	2
T^4	59.4	0.3	61	62	63	3	60	2
T ⁶	-293.4	2.2	-291	-290	-292	5	-293	4
T^7	348.5	3.7	347	352	358	8	349	7
T^8	348.8	4.0	355	363	354	11	355	
EAVE	24,178	1	24,176	24,176	24,186	3	24,178	5
σ	8.1	l	9.4	7.4	8.1		8.9)
Np	20)	20	24	20		20	
N _{expt}	12	7	127	118	101	l	127	7

^a Refer to the caption in Table 1.

fairly similar to those given above. The fitted value of M^0 from Ref. [24] is very uncertain (with more than 50% error) and that for P^2 differs from ours by 10% which is much higher than the average 1% discrepancies found for most of the other parameters. The most likely reason is that their fits omitted H_{SS} in their full Hamiltonian and so their fitted values of M^k and P^k were distorted to absorb the effects of that interaction.

The last two columns in Table 2 present the observed and calculated Zeeman splittings, using our best fit parameter values (Table 1). The observed values were reported by Dieke and Eisenstein, and the agreement of the calculation is reasonable.

3.2. 4f³:Nd³⁺

We follow the notation of Krämer et al. [39] for labeling the irreps of the Kramers doublet energy levels of Nd^{3+} in the C_{3h} double

Table 4

Observed (4 K [41]) and calculated energy levels for selected multiplets of Nd³⁺ in LaCl₃.^a

No.	SLJ	2μ	C _{3h} irrep	Eobs	Δ	s _{obs}	$ S^{(1)} _{calc}$	$ s^{(1)} + s^{(2)} _{calc}$
1	⁴ I _{9/2}	5	В	0	5.8	4.01(1)	4.20	4.03
2		1	Α	115.4	7.5	0.62	0.72	0.82
3		3	С	123.2	-0.1	3.15	3.41	3.44
6	$4I_{11/2}$	3	С	1973.9	1.0	7.46	7.74	7.47
7		1	Α	2012.6	0.9	5.54	4.16	4.18
8		5	В	2026.9	4.3	4.34	4.32	4.31
9		1	Α	2044.2	-0.9	7.25	5.50	5.63
10		3	С	2051.6	3.4	1.66	1.95	1.94
48	² H(2) _{11/2}	3	С	15907.1	-15.7	9.14(4)	7.18	7.17
49		5	В	15923.9	-2.8		0.98	0.97
50	*	1	Α	15948.1	12.6	0.9(3)	2.75	2.75
51		3	С	15953.0	1.7		0.61	0.58
52	*	1	Α	15960.8	4.3	11.7(4)	11.96	11.96
57	⁴ G _{7/2} *	3	С	17228.8	-4.2	2.69	2.81	2.88
58		5	В	17248.0	-5.8		0.71	0.89
59		5	В	17287.0	-7.1		0.35	0.02
60	*	1	Α	17297.4	10.9	0.1	0.88	0.18
65	${}^{4}G_{9/2}$	5	В	19425.6	3.1		0.80	0.63
66		1	Α	19430.9	-2.7	0.7(1)	5.78	5.73
67		3	С	19434.8	-1.5	9.89(7)	10.07	10.07
68		3	С	19454.6	8.6	2.42	2.50	2.39
69		5	В	19458.7	-0.5	2.8(7)	3.30	3.48
152	$^{2}H(1)_{11/2}*$	1	Α	34,043	2.0	6.8	7.13	7.08
153	² D _{5/2} *	3	С	34,048	3.2	2.85	3.31	3.31
154	*	5	В	34110.7			2.38	2.39
155	$^{2}H(1)_{11/2}$	3	С	34118.7			0.77	0.79
156	² D _{5/2} *	1	А	34,127	6.2	2.2	1.91	1.85
157	$^{2}H(1)_{11/2}$	5	В	34150.1			0.88	0.90
158	*	1	А	34.235	2.7		0.42	0.47
159		3	С	34264 1			5.40	5.43
163	${}^{2}F(2)_{7/2*}$	5	В	20576.6			1.83	185
164	· (-)//2·	1	Δ	39.637	16.2		1.00	1.02
165	*	1	л р	20,027	10.2		1.14	1.00
105	*	5	D	<u>39626.0</u>	17.0		4.11	4.15
166	*	3	C	39,664	17.3		3.43	3.45

^a Refer to the footnote in Table 2. Underlined values are calculated energies. The Zeeman $|s|_{obs}$ values are from Refs. [44–46]. Where several different values were reported, the mean is given and the figure in brackets represents the ±error on the last digit.

Table 5				
Energy parameters	for	Er ³⁺	in	LaCl ₃ . ^a .

Ref. parameter	This wor	·k	Ref. [39]	b	Ref. [24]		Ref. [26]
B ₂₀	181.8	7.1	181.5	16	199.1	14.6	216
B ₄₀	-246.8	9.3	-268.6	20	-317.3	21.3	-271
B ₆₀	-426.8	5.4	-414.1	16	-401.6	15.7	-411
B ₆₆	276.2	3.7	274.8	13	239.6	14.1	272
F^2	97,384	74	98,260	45	98,220	43	98,203
F^4	70,095	163	69,793	62	70,079	59	69,647
F^6	55,282	237	48,114	71	49,625	65	49,087
ζf	2375.1	0.4	2362	3	2364	5	2370
M ⁰	4.27	0.06	4.2	1.4	3.56	1.94	4.5
P^2	727	20	416	20	381	32	667
α	15.62	0.07	17.4	1.7	16.06	1.79	15.9
β	-646	3	-638	10	-607	11	-632
γ	1181	59	2061	38	1787	35	[2017]
T^2	290	10	426	19	286	21	300
T^3	49.0	0.8	48	5	48	6	48
T^4	4.2	1.6	22	7	14	8	18
T^6	-339	5	-305	13	-324	11	-342
T^7	228	9	289	17	172	19	214
T^8	476	11	353	18	323	22	449
EAVE	35,544	6	35,459	12	35,468	11	35,490
σ	7.	.0	9		10	.5	
N_p	2	0	21		20)	
N _{expt}	8	3	73		83	3	

^a Refer to the caption in Table 1. The ratios $M^{0}:M^{2}:M^{4}$ and $P^{2}:P^{4}:P^{6}$ were fixed as 1.00:0.56:0.38 and 1.00:0.75:0.50, respectively in this work.

 b Additional parameter $G^{4}_{10A0} = 194 \pm 31 \ cm^{-1}$ for the orthogonal CCF operator.

group [40] where $(\Gamma_7 + \Gamma_8)$, $(\Gamma_9 + \Gamma_{10})$ and $(\Gamma_{11} + \Gamma_{12})$ are represented briefly as *A*, *B* and *C*, respectively. The selection rules for

electric dipole and magnetic dipole transitions have previously been tabulated [39]. For the system LaCl₂:Nd³⁺, 127 levels were assigned by Pelletier-Allard et al. [41], enlarging the dataset of the earlier study by Crosswhite et al. [42]. Crosswhite's calculation [42] included spin-spin interaction and utilized 20 parameters to fit 101 levels with a mean error of 8.1 cm^{-1} , and is in agreement with our calculation using their parameters (there are two typographical sign errors in the tabulation of reduced matrix elements in Ref. [43]). We are unable to repeat the calculation of Pelletier-Allard et al. [41] although their energy parameters do not differ greatly from ours. Our initial fit to Pelletier-Allard's experimental data for 127 levels using 20 parameters gave the r.m.s. error of 6.7 cm⁻¹, but the symmetry irreps for levels 49,50; 59,60; 65,66 and 164,165 were reversed in each case. This prompted a closer scrutiny of the energy levels, together with the abundant experimental Zeeman splitting data reported by Carlson and Dieke [44], Rana et al. [45], and Eisenstein [46]. Energy levels of some selected multiplets from the revised fit are given in Table 4, with the parameter values listed in Table 3. On comparing the fitted values of the parameters from the present work with those of Tröster et al. [38], agreement (with less than 0.5% discrepancy) is found for most parameters except for the P^k and M^j parameters and some T^s (s = 2 and 8) parameters.

By contrast to the observations for Pr^{3+} , the free variation of M^k and P^k parameters in our calculations gave a good fit for LaCl₃:Nd³⁺, with other parameter values not greatly shifted from those given in Table 3. The fitted values were obtained as $M^0 = 1.666 (M^0:M^2:M^4$ was 1.00:0.75:0.44) and $P^2 = 232.0 (P^2:P^4:P^6$ was 1.00:0.47:0.21). Several calculations for the LaCl₃:Nd³⁺ system have utilized the correlation CF and the fitting is not appreciably different although

Table 6	
Observed (4 K $[39,47-49]$) and calculated energy levels for selected multiplets of Er^{3+} in LaCl ₃	a

No.	SLJ	2μ	C _{3h} irrep	Eobs	Δ	Ref.	$ s^{(1)} _{calc}$	S _{obs}	$ S_x _{calc}$	$ S_x _{obs}$
1	$4I_{15/2}$	5	В	0	11.2	[49]	2.20	1.99 ^b	8.8	8.76 ^b
16	${}^{4}I_{11/2}*$	3	С	10207.5	-2.8	[49]	2.50		0.0	
17	*	5	В	10209.1	-0.2	[49]	3.22		3.6	
18	*	1	А	10210.5	-3.8	[49]	0.05		5.4	
19	*	5	В	10222.0	-5.3	[49]	5.20		3.6	
20	*	1	А	10226.7	-4.1	[49]	9.84		0.5	
21	*	3	С	10240.6	-8.0	[49]	8.44		0.0	
34	² H(2) _{11/2*}	5	В	<u>19113.9</u>			0.26		5.8	
35	*	3	С	19135.1	-10.1	[48]	0.57	0.78	0.0	0.34
37	*	1	А	19140.4	-12.0	[48]	10.84	7.73	0.8	2.72
38	**	3	С	19161.1	-14.1	[48]	7.38	3.23	0.0	0.36
39	*	1	А	19178.3	1.6	[48]	0.55	1.29	6.0	
60	${}^{4}G_{9/2}$	5	В	27346.1	2.0	[49]	5.10		3.6	
61	*	3	С	27361.3	5.4	[49]	0.47		0.0	
62		1	Α	27367.4	13.9	[49]	1.11		5.5	
64		3	С	27370.1	7.1	[49]	7.13		0.0	
65	² K _{15/2}	1	А	27601.3	-3.8	[49]	1.03		8.5	
66		3	С	27624.0	2.1	[49]	3.05		0.0	
73	⁴ G _{7/2} *	5	В	27987.9			5.54		1.5	
74	*	1	А	27990.7	-2.9	[49]	0.96		3.8	
75	*	5	В	27998.2			3.62		1.5	
76	*	3	С	27994.5	-6.5	[49]	2.86		0.0	
79	² K _{13/2}	1	А	32899.6	9.1	[49]	0.98		6.4	
80	,	3	С	32920.9	17.8	[49]	2.77		0.0	
85		1	А	33033.5	8.8	[49]	1.62		0.9	
94	² D(1) _{5/2*}	5	В	34740.3			6.02		0.0	
95	*	1	А	34754.8	2.3	[49]	1.21		3.6	
96	*	3	С	34771.0	9.1	[49]	3.61		0.0	
109	${}^{2}I_{11/2}*$	3	С	40830.2	-9.1	[49]	5.92		0.0	
110	*	1	А	40846.2	1.1	[49]	0.63		5.7	

^a Refer to the footnote in Table 2. Underlined values are calculated energies. The Zeeman values are from Ref. [48]: *s*_{obs} and *s*_x are in Lorentz units and refer to the magnetic field orientation parallel and perpendicular to the crystal axis, respectively.

^b Ref. [50] for the observed values.

rather more parameters are involved, as shown for example by Ref. [24] in Table 3.

The *J*-mixing effect is important for many multiplets of Nd³⁺. In particular, there are shifts of -117 cm^{-1} and $+70 \text{ cm}^{-1}$ for the barycenters of ${}^{2}\text{D}(2)_{5/2}$ and ${}^{2}\text{H}(1)_{11/2}$, respectively, when *J*-mixing is turned on. By contrast, if the calculation is repeated without the inclusion of spin–spin interaction, the free ion energies are shifted by different amounts: -105 cm^{-1} and 64 cm^{-1} , respectively. Thus the spin–spin interaction has an effect upon the *J*-mixing between different multiplets and the impact can be appreciable in some cases.

3.3. 4f¹¹:Er³⁺

The energy levels of Er³⁺ in LaCl₃ were investigated via absorption and luminescence by Eisenstein [47], Dieke and Singh [48], Varsanyi and Dieke [49], and more recently by Krämer et al. [39]. The latter authors noted that their experimental results were in agreement with earlier studies, but some differences with other datasets are apparent. The dataset in Table 6 is mainly from Varsanyi and Dieke [49] and is more accurate. First, the lowest level of ${}^{4}I_{11/2}$ is clearly at 10207.5 cm⁻¹ from the emission spectra presented by Varsanyi and Dieke (Table 2, [49]) and Dieke and Singh (Table 3, [48]). The additional levels of ${}^{4}G_{9/2}$, ${}^{2}K_{15/2}$, ${}^{4}G_{7/2}$, $^2\text{K}_{13/2},\,^2\text{D}(1)_{5/2},\,^2\text{I}_{11/2}$ not reported by Krämer et al. [39] are taken from bands reported by Dieke and Singh [48], and exhibit the correct polarizations. The irreps of experimental levels at 40830.2 cm⁻¹ and 40846.2 cm⁻¹ have been interchanged from those given by Varsanyi and Dieke [49] since no polarization data are available; and for levels at 34754.8 cm^{-1} and 34771.0 cm^{-1} since the polarization data are ambiguous [49]. There are calibration differences for bands reported by Eisenstein [47] and Varsanyi and Dieke [49], although there is agreement otherwise. For example, there is a systematic difference of 11.2 cm^{-1} for the four reported ${}^{2}\text{H}_{11/2}$ bands. The absorption transitions from the ${}^{4}\text{I}_{15/2}$ B ground state to the two levels (B) of ${}^{2}\text{H}(2)_{11/2}$ are electric dipole forbidden.

We are unable to repeat the calculation of Krämer et al. [39], probably because they used the reduced matrix elements for the conjugate configuration $4f^3$ in which the t_2 operator contains some two-electron contributions correlated with the Slater's operators f_k . Besides, our fitted values of P^2 , γ and T^4 are significantly different from those of other fits. Higher energy levels observed by Varsanyi and Dieke [49] which have been included in the present calculation were omitted by Kramer et al. [39] because they could not be satisfactorily fitted. For example, the observed levels 79, 80 (${}^2K_{13/2}$) [49] were calculated at 55.6 cm⁻¹ and 64.3 cm⁻¹ to lower energy, respectively by Kramer et al., and observed levels 95, 96 (${}^2D_{5/2}$) [49] were calculated at 118.1 cm⁻¹ and 119.5 cm⁻¹ to lower energy, respectively.

When a kind of CCF effect is included in the fit, the r.m.s. error, σ , of the fit is reduced by 0.1, 0.5 and 0.6 cm⁻¹ for the OCCF, SCCF and LCCF, respectively. However, if the spin–spin interaction H_{ss} is not included, then the r.m.s error will increase by 1.5 cm⁻¹, showing that the results of any CCF fit without H_{ss} are quite questionable. The calculated values of Zeeman splittings $s^{(1)}$ and s_x (in Lorentz units) compare favorably with the observed values from Refs. [48,50] for the magnetic field orientation parallel and perpendicular to the crystal axis, respectively.

Finally, the calculation was carried out with free variation of M^k or P^k . The values of other parameters were not greatly changed and the fitted values (in cm⁻¹) were $M^0 = 4.285$ ($M^0:M^2:M^4 = 1.00:0.83:0.25$), and $P^2 = 674.1$ ($P^2:P^4:P^6 = 1.00:0.87:0.39$). This indicates an increasing trend for M^2 with respect to M^0 on going from Pr to Nd to Er. Also, there is a linear relation ($R^2_{adi} = 0.993$, for a plot of M^0 versus

number, N, of $4f^N$ electrons for these three lanthanides. A complete analysis for the entire lanthanide series will be of interest to ascertain if parameter variations do occur in a smooth manner, and this will be subsequently performed.

4. Conclusions

The experimental energy level datasets for the LaCl₃:Ln³⁺ series are the most accurate available at present. However, following the early studies there have been few reports to fill in incomplete or uncertain levels in these datasets. For example, the energy levels of Yb³⁺ in LaCl₃:Yb³⁺ have not yet been studied. The higher multiplets of Nd³⁺, calculated to begin at 47,264 cm⁻¹ (${}^{2}G(2)_{9/2}$) and 65,640 cm⁻¹ (${}^{2}F(1)_{7/2}$) are separated by large gaps (calculated as 7618 cm⁻¹ and 17,306 cm⁻¹, respectively) from the next lower ones and should be luminescent, except that the higher multiplet lies within the conduction band. The energy levels of Er^{3+} above 27,600 cm⁻¹ are sketchy. The $Er^{3+} {}^{4}D_{1/2}$ level (~46,710 cm⁻¹) is calculated at \sim 3300 cm⁻¹ above the next lowest level and should be luminescent. The levels of Eu³⁺ and Tb³⁺ are restricted to lower multiplets and two-photon studies would yield more complete energy level datasets. Part of the failure to conduct further experimental studies into these systems may result from the conception that everything is well-understood. Also, the hygroscopic nature of LaCl₃ crystals hinders technical applications. It is hoped that more experimental work to extend these energy level datasets could be forthcoming. On the theoretical side, we have noted that we are unable to repeat most of the energy level calculations for the LaCl₃:Ln³⁺ systems. This is partly due to calculation errors and/or to some errors in matrix elements which were previously pointed out [12]. In many cases, especially for the surveys of parameter values across the lanthanide series, it is not clear exactly which energy levels were fitted, and if the level irreps and/or g values were taken into account in the calculations. As advocated by Judd and Crosswhite [51], the use of orthogonal operators can help to reduce the dataset dependence of fitted values of parameters so that the comparison of fits by various researchers will become more meaningful. Spin-spin interaction was included in the semi-empirical Hamiltonian only for the cases of LaCl₃ doped with Pr^{3+} and Nd^{3+} studied by Crosswhite et al. [26,42]. Its absence in other systems may have led to some other energy parameters taking on strange values. The energy level fits presented herein have good reliability, as also demonstrated by the agreement with Zeeman data, and by their accuracy. The inclusion of the spin-spin interaction into the energy Hamiltonian can lead to appreciable shifts of multiplet levels, for example the shift of 20 cm^{-1} for $\text{Pr}^{3+3}\text{P}_0$, which is the same order as correlation CF corrections. Moreover, the shifts are very different for different terms, as expected from the relevant selection rules. Subtle effects, such those due to J-mixing, have been identified in this study.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2013. 04.056.

References

- [1] B. Wybourne, Spectroscopic Properties of Rare Earths, Wiley, New York, 1965. [2] R.D. Cowan, The Theory of Atomic Structure and Spectra, University of
- California, Berkeley, CA, 1981. [3] C. Görller-Walrand, K. Binnemans, in: K.A. Gschneidner Jr., L. Eyring (Eds.),
- [5] C. Ooner Wahand, R. Binneman, M. K.P. Oschnetater Jr., E. Byrng (eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 23, Elsevier Science BV, Amsterdam, 1996, pp. 121–283 (Chapter 155).
- [4] D.J. Newman, B. Ng (Eds.), Crystal Field Handbook, Cambridge University Press, Cambridge, 2000.
- [5] L. Hu, M.F. Reid, C.-K. Duan, S. Xia, M. Yin, J. Phys.: Condens. Matter. 23 (2011) 045501.
- [6] P. Novák, J. Kuriplach, Phys. Rev. B 50 (1994) 2085.
- [7] Y. Shen, K.L. Bray, Phys. Rev. B 58 (1998) 5305.
- [8] H. Crosswhite, D.J. Newman, J. Chem. Phys. 81 (1984) 4959.
- [9] Y.Y. Yeung, D.J. Newman, J. Chem. Phys. 86 (1987) 6717.
- [10] M.F. Reid, J. Chem. Phys. 87 (1987) 2875.
- [11] B.R. Judd, E. Lo, J. Phys.: Condens. Matter. 6 (1994) L799.
- [12] X.Y. Chen, G.K. Liu, J. Margerie, M.F. Reid, J. Lumin. 128 (2008) 421.
- [13] J.R.G. Thorne, M. Jones, C.S. McCaw, K.M. Murdoch, R.G. Denning, N.M. Khaidukov, J. Phys.: Condens. Matter. 11 (1999) 7851.
- [14] B.R. Judd, Phys. Rev. Lett. 39 (1977) 242.
- [15] D.J. Newman, G.G. Siu, W.Y.P. Fung, J. Phys. C: Solid State Phys. 15 (1982) 3113.
- [16] E. Rukmini, C.K. Jayasankar, M.F. Reid, J. Phys. Condens. Matter. 6 (1994) 5919.
- [17] D. Garcia, M. Faucher, J. Chem. Phys. 90 (1989) 5280.
- [18] D. Garcia, M. Faucher, J. Chem. Phys. 91 (1989) 7461.
- [19] Y.Y. Yeung, Atomic Data and Nuclear Data Tables, submitted for publications.
- [20] H.U. Rahman, Il Nuovo Cimento D 15 (1993) 1273.
- [21] H.M. Crosswhite, H. Crosswhite, W.T. Carnall, K. Rajnak, J. Chem. Phys. 67 (1977) 3002.
- [22] B.R. Judd, H.M. Crosswhite, H. Crosswhite, Phys. Rev. 169 (1968) 130.
- [23] C.A Morrison, R.P Leavitt, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 5, North-Holland, Amsterdam, 1982, pp. 461–692 (Chapter 46).
- [24] C.K. Jayasankar, F.S. Richardson, M.F. Reid, J. Less Common Met. 148 (1989) 289.
- [25] M.M. Curtis, D.J. Newman, G.E. Stedman, J. Chem. Phys. 50 (1969) 1077.
- [26] H.M. Crosswhite, Colloques Internationaux C.N.R.S. No. 255: Spectroscopie des Éléments de Transition et des Éléments Lourds dans les Solides (1977) 65–69.
- [27] G. Burns, J. Chem. Phys. 42 (1965) 377.
- [28] C. Delsart, N. Pelletier-Allard, R. Pelletier, Opt. Commun. 16 (1976) 114.
- [29] B.R. Judd, H.T. Wadzinski, J. Math. Phys. 8 (1967) 2125.
- [30] V.L. Donlan, Bull. Am. Phys. Soc. II (14) (1969) 939.
- [31] J.L. O'Hare, V.L. Donlan, Phys. Rev. 185 (1969) 416.
- [32] J.L. O'Hare, V.L. Donlan, Phys. Rev. B 14 (1976) 3732.
- [33] J.L. O'Hare, V.L. Donlan, Phys. Rev. B 15 (1977) 10.
- [34] R. Sarup, M.H. Crozier, J. Chem. Phys. 42 (1965) 371.
- [35] R.S. Rana, F.W. Kaseta, J. Chem. Phys. 79 (1983) 5280.
- [36] J.S. Margolis, J. Chem. Phys. 35 (1961) 1367.
- [37] R.S. Rana, C.D. Cordera-Montaldo, N. Bloembergen, J. Chem. Phys. 81 (1984) 2951.
- [38] Th. Tröster, T. Gregorian, W.B. Holzapfel, Phys. Rev. B 48 (1993) 2960.
- [39] K.W. Krämer, H.U. Güdel, R.N. Schwartz, Phys. Rev. B 56 (1997) 13830.
- [40] G.F. Koster, J.O. Dimmock, R.G. Wheeler, H. Statz, Properties of the Thirty Two Point Groups, MIT Press, Cambridge, MA, 1963. Table 57.
- [41] N. Pelletier-Allard, R. Pelletier, J. Shertzer, J. Chem. Phys. 93 (1990) 14.
- [42] H.M. Crosswhite, H. Crosswhite, F.W. Kaseta, R. Sarup, J. Chem. Phys. 64 (1976) 1981.
- [43] H. Crosswhite, H.M. Crosswhite, B.R. Judd, Phys. Rev. 174 (1968) 89.
- [44] E.H. Carlson, G.H. Dieke, J. Chem. Phys. 34 (1961) 1602.
- [45] R.S. Rana, F.W. Kaseta, R.H. Garvey, J. Chem. Phys. 77 (1982) 4400.
- [46] J.C. Eisenstein, J. Chem. Phys. 39 (1963) 2134.
- [47] J.C. Eisenstein, J. Chem. Phys. 39 (1963) 2128.
- [48] G.H. Dieke, S. Singh, J. Chem. Phys. 35 (1961) 555.
- [49] F. Varsanyi, G.H. Dieke, J. Chem. Phys. 36 (1962) 2951.
- [50] E.H. Wong, J. Chem. Phys. 34 (1961) 1989.
- [51] B.R. Judd, H. Crosswhite, J. Opt. Soc. Am. B1 (1984) 255.