Correlation-crystal-field analysis of $Nd^{3+}(4f^3)$ energy-level structures in various crystal hosts

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Abstract. We have performed an in-depth correlation-crystal-field (CCF) analysis of the energy-level structures in 10 $Nd^{3+}(4f^3)$ crystal systems: NdF_3, $Nd_2Te_4O_{11}$, $NdVO_4$, $NdPO_4$, Nd^{3+}:$LiYF_4$, Nd^{3+}:$LaVO_4$, Nd^{3+}:$LaCl_3$, Nd^{3+}:BaY_2F_8, Nd^{3+}:$YAlO_3$ and Nd^{3+}:$LuAlO_3$. A model Hamiltonian employing 20 free-ion parameters, appropriate one-electron crystal-field interaction parameters and also selected two-particle CCF interaction parameters was diagonalized within the complete 364 $SLJM_J$ basis set of the $4f^3$ electronic configuration. Inclusion of the fourth-rank $g_2^{(4)}$, $g_{10A}^{(4)}$ and $g_{10B}^{(4)}$ CCF operators in the phenomenological energy-level fits yields an overall improved agreement between calculated and empirical energy levels besides eliminating major discrepancies between calculated and observed crystal-field splittings within the *anomalous* $^2H(2)_{11/2}$ multiplet of Nd^{3+} ion. The fits are also in qualitative agreement with the *ab initio* calculations of CCF effects for lanthanide ions.

1. Introduction

The locations and assignments of the energy levels from the discrete electronic spectra of the $4f^N$ configurations in solids are in general well calculated using a model Hamiltonian that involves the adjustment of both free-ion and crystal-field parameters [1–16]. The model often gives a good fit to most of the data, but certain 'anomalous' multiplets remain poorly fitted [17–24]. Notably $^1D_2$ of Pr^{3+} [18], $^2H(2)_{11/2}$ of Nd^{3+} [21], $^5D_1$ and $^5D_2$ of Eu^{3+} [23], $^6I_{17/2}$ of Gd^{3+} [24], $^3K_8$ of Ho^{3+} [24] and $^1G_4$ and $^1D_2$ of Tm^{3+} [13] multiplets remain poorly fitted when the one-electron crystal-field parameters are optimized using all the observed energy levels. When a similar pattern exists for a particular lanthanide ion in many different crystal hosts, it is clear that either new insights on the missing interaction mechanism may be looked into in detail or the model Hamiltonian needs to be extended beyond the one-electron crystal field.

Garcia and Faucher [17–19] identified the missing interaction as configuration interaction due to the excited configurations and suggested including the excited configuration $4f^{N-1}5d^1$ together with the ground configuration $4f^N$ for the crystal-field analysis of trivalent lanthanides. The abnormal behaviour of the $^1D_2$ level of Pr^{3+}:$PrCl_3$ has been removed considerably [18] by taking into account the configuration interaction between $4f^2$ and $4f^15s^1$ through the odd-rank crystal-field parameters. Later on [19], the discrepancy between experimental and calculated splitting of $^1D_2$ multiplet has been completely eliminated by taking into account the multiconfiguration-interaction effects ($4f^16s^1$ and $4f^16p^1$) on the ground configuration ($4f^2$) for Pr^{3+}:$PrCl_3$. This parametrization scheme has the difficulty of being applied to configurations other than f^2 and f^3 configurations, since f^3 itself is a

complicated system due to the size of the problem—364 levels for the ground configuration $4f^3$ and 910 levels for the next excited configuration $4f^2 5d^1$. The same group has treated this problem in a different way by modifying the reduced matrix elements for the abnormal multiplets $^2H(2)_{11/2}$ of Nd^{3+} [21], $^2H(2)_{11/2}$ of Er^{3+} [22] and $^5D_1$ and $^5D_2$ of Eu^{3+} [23] and obtained a good fit for the abnormal multiplets without affecting other multiplets. The modification of the reduced matrix elements is only a mathematical trick and failed to identify any specific interaction that allows one to modify the reduced matrix elements.

On the other hand, modification of the one-electron crystal field for the analyses of lanthanide spectra has been suggested by Judd [25, 26], and has been applied to several systems with satisfactory results [12–14, 24, 27–35]. Modification of the one-electron crystal field involves the inclusion of spin-correlated crystal field (SCCF) or correlation crystal field (CCF) due to many-electron (correlation) effects in the model Hamiltonian, where the former considers few orthogonal operators and the latter considers all possible orthogonal operators. The SCCF operators are simply related to a small number of CCF operators. Yeung and Newman [36] identified the orbitally correlated crystal-field (LCCF) parametrization, and the analysis of SCCF and LCCF for Pr^{3+}:$LaCl_3$ and Er^{3+}:$LaCl_3$ yields that SCCF effects are more influential than LCCF effects. CCF parametrization is preferable to SCCF analyses since the CCF analyses involve consideration of all the possible orthogonal correlation operators and also CCF analyses are in agreement with the *ab initio* calculations [37].

The construction of orthogonal operators to represent CCF effects in the f^N configuration of lanthanide and actinide ions is discussed and is emphasized from the energy-level analysis of Ho^{3+}:$LaCl_3$ and Gd^{3+}:$LaCl_3$ [31]. The $g_3^{(6)}$ operator was found to be useful to correct the anomalous multiplets $^3K_8$ of Ho^{3+} and $^6I_{17/2}$ of Gd^{3+} [31]. The anomalous $^2H(2)_{11/2}$ multiplet of Nd^{3+}:$Y_3Al_5O_{12}$, $LaCl_3$, $LiYF_4$, LaF_3, $NdAlO_3$ and $Na_3[Nd(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$ has been investigated, and it is suggested that correlation effects represented by the $g_2^{(4)}$, $g_{10A}^{(4)}$ and $g_{10B}^{(4)}$ operators could correct the problem [32]. The same CCF operators were used to analyse the energy-level schemes of $Nd(H_2O)_9(CF_3SO_3)_3$ and Nd^{3+}:$CsCdBr_3$ [35]. Similar results were obtained for Er^{3+} in various crystal hosts [38, 39]. CCF analysis for an actinide compound (Np^{3+}:$LaCl_3$) reveals that the operators $g_{10A}^{(4)}$, $g_{10B}^{(4)}$, $g_{10}^{(2)}$ and $g_4^{(4)}$ have a significant influence on the energy-level fit [34]. Line-strength analysis using the eigenvectors from a CCF fit yields an improved fit for Nd^{3+}:$Y_3Al_5O_{12}$ [40], particularly for the anomalous multiplets (such as $^2H(2)_{11/2}$) for which the crystal-field fit is improved.

The splitting of the ground multiplet of Gd^{3+} is of interest because it is dominated by effects that are normally masked by the one-electron crystal field, such as the relativistic crystal-field and correlation effects [31]. It has been suggested that the SCCF has an important effect on this multiplet, but an attempt to include appropriate values for the $k = 2$ SCCF in the parametrization of the Gd^{3+}:$LaCl_3$ spectrum yields unsatisfactory results. In some way this is unfortunate, since parameter fits to the optical spectrum may not give us any information about the parameters affecting the ground-state splitting. Nevertheless, Gd^{3+} *is particularly interesting because the diagonal matrix elements of the one-electron crystal-field operators vanish.* Therefore correlation and relativistic effects are expected to be more prominent.

In the studies of Nd systems, it has been found that it is necessary to obtain more refined Hamiltonians and crystal-field eigenvectors than have previously appeared in the literature before carrying out intensity calculations [35]. The crystal-field eigenvectors are usually obtained from semiempirical energy-level calculations in which a parametrized model Hamiltonian is used to fit calculated versus empirical energy-level data. The eigenvectors of the optimally parametrized model Hamiltonian are then used as basis vectors in the

subsequent intensity calculations [41, 42]. The details of the model Hamiltonian determine the $SLJM_J$ compositions of the crystal-field eigenvectors and the transition intensities are extraordinarily sensitive to these $SLJM_J$ compositions.

We have also noticed that the crystal-field levels were not analysed with a uniform free-ion part of the model Hamiltonian. For example, Gruber, Morrison *et al* [43–45] and Lakshman *et al* [46] have never considered the T^i, M^j and P^k parameters; Caro, Porcher and Faucher's group [9, 11, 16, 21] have not considered the M^j and P^k parameters; whereas Richardson [8, 13, 14, 28, 30, 41, 42], Reid [12, 31–34] and Carnall *et al* [15] took all the parameters into consideration. In order to have a meaningful comparison and discussion of atomic parameters in different environments, it is always preferable to use a uniform $\hat{H}_A$ model. As mentioned above, it is essential to reanalyse the Nd energy-level data with a uniform model Hamiltonian that includes CCF operators in the crystal-field model Hamiltonian. In this paper, we report results obtained from the new energy-level analyses carried out for Nd^{3+} in 10 different hosts (or compounds). The systems are NdF$_3$, Nd$_2$Te$_4$O$_{11}$, NdVO$_4$, NdPO$_4$, Nd^{3+}:LiYF$_4$, Nd^{3+}:LaVO$_4$, Nd^{3+}:LaCl$_3$, Nd^{3+}:BaY$_2$F$_8$, Nd^{3+}:YAlO$_3$ and Nd^{3+}:LuAlO$_3$.

The main objectives of the present study are: (i) to obtain an improved and more accurate characterization of the 4f^3 energy parameters for Nd^{3+} ion in the 10 systems identified above; (ii) comparison of the phenomenological atomic (free-ion) and crystal-field parameter values across the 10 systems; (iii) comparison of the results obtained without and with the inclusion of CCF interactions; (iv) comparison of calculated versus observed crystal-field levels within the 'anomalous' ^{2}H(2)$_{11/2}$ multiplet; and (v) comparison of the ratios of phenomenological two-particle crystal-field parameters to one-particle crystal-field parameters of equal rank with that of *ab initio* calculations.

2. Energy-level fits

The model Hamiltonian used in this study can be written as [3, 30–37]

$$\hat{H} = \hat{H}_A + \hat{H}_{CF} + \hat{H}_{OCCF} \tag{1}$$

where $\hat{H}_A$ contains the isotropic (atomic) parts of $\hat{H}$, $\hat{H}_{CF}$ the one-electron part of the crystal-field interactions and $\hat{H}_{OCCF}$ the correlation (many-electron) crystal-field interactions.

The $\hat{H}_A$ operator is defined as [3]

$$\hat{H}_A = E_{\text{ave}} + \sum_k F^k \hat{f}_k + \xi_{\text{SO}} \hat{A}_{\text{SO}} + \alpha \hat{L}(\hat{L} + 1) + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7)$$

$$+ \sum_i T^i \hat{t}_i + \sum_j M^j \hat{m}_j + \sum_k P^k \hat{p}_k \tag{2}$$

where $k = 2, 4, 6$; $i = 2, 3, 4, 6, 7, 8$; $j = 0, 2, 4$. The various operators ($\hat{f}_k$, $\hat{A}_{\text{SO}}$, $\hat{L}$, $\hat{G}$, $\hat{t}_i$, $\hat{m}_j$ and $\hat{p}_k$) and parameters (E_{ave}, F^k, ξ_{SO}, α, β, γ, T^i, M^j and P^k) in equation (2) are defined and explained in detail in the literature [1–3]. The parameters are defined as central field (E_{ave}), two-body electrostatic repulsion (F^k), two-body configuration (α, β, γ), three-body configuration (T^i), spin–orbit (ξ), spin–other-orbit (M^j) and electrostatically correlated spin–orbit (P^k) interactions.

Most of the analyses of energy levels of the lanthanide $4f^N$ configuration use a one-electron crystal-field Hamiltonian to model the interaction of the 4f electrons with the ligands as [1–16]

$$\hat{H}_{\text{CF}} = \sum_{k,q} B_q^k C_q^{(k)} \tag{3}$$

where

$$C_q^{(k)} = \sum_i C_q^{(k)}(i) \tag{4}$$

and $C_q^{(k)}(i)$ is a spherical tensor operator for the ith f electron. The k and q are symmetry-dependent labels: $k = 2, 4, 6$ and $q = -k \leqslant q \leqslant k$. The $B_q^k (B_{kq})$ are phenomenological one-particle crystal-field parameters.

To take into account the correlation (many-electron) effects, one requires two-body operators. It is possible to write a general parametrization in the form [27, 33]

$$\hat{H}_{\text{CCF}} = \sum_{k_1, k_2, K} B_Q^K(k_1, k_2) \sum_{i>j} [u^{(k_1)}(i) u^{(k_2)}(j)]_Q^{(K)} \tag{5}$$

where the $u^{(k)}$ are unit tensor operators and i and j label the f electrons. The quantum numbers k_1 and k_2 can range from 0 to 6, K can run through the even integers from 0 to 12, and Q takes values from -12 to $+12$ including zero. B_Q^K are phenomenological two-particle crystal-field parameters.

The parametrization of equation (5) can be thought of as an extension of Coulomb interaction (F^k, $k = 2, 4, 6$) to take into account non-spherically symmetric effects. These operators have the disadvantage of not being orthogonal over the f^N configuration. Judd [26] has given an alternative parametrization, which is an extension of Racah's E^i parameters. In Judd's notation the orthogonal CCF is written as

$$\hat{H}_{\text{OCCF}} = \sum_{i, K, Q} G_{iQ}^K g_{iQ}^{(K)}. \tag{6}$$

Judd's OCCF operators have several advantages. Unlike the operators in equation (5), OCCF operators are orthogonal over the f^N configuration. They also have well defined transformation properties under the parentage groups used to label the states of f^N (U_{14}, etc) [26, 31].

A serious problem with the parametrization of either equation (5) or equation (6) is the number of extra parameters that need to be considered. There are 43 CCF or OCCF parameters [31–33]. The enormous number of possible parameters makes simply adding them to the fit completely impracticable. In order to make progress, the only possible approach seems to be to seek out features of the spectra that are particularly sensitive to certain operators, as carried out for Gd^{3+} [31], Nd^{3+} [32] and Np^{3+} [34] energy-level analysis. Li and Reid [32] found that the $G_2^{(4)}$, $G_{10A}^{(4)}$ and $G_{10B}^{(4)}$ parameters were particularly important for the $^2H(2)_{11/2}$ *anomalous* multiplet of Nd^{3+}.

Thus the analysis of energy-level data of Nd^{3+} systems has been carried out by using the model Hamiltonian (equation (1)) that consists of 20 free-ion parameters (equation (2)), appropriate one-electron crystal-field parameters (equation (3)) plus three CCF parameters ($G_2^{(4)}$, $G_{10A}^{(4)}$ and $G_{10B}^{(4)}$ of equation (6)).

3. Calculations

All energy-level calculations were carried out by diagonalizing the total (atomic plus crystal-field) Hamiltonian within the complete $SLJM_J$ basis set of the 4f^3 electronic configuration. In our parametric fits of calculated to experimental energy-level data, 16 of the 20 parameters in $\hat{H}_A$ (equation (2)) were used as independent fitting variables. Four of the atomic parameters, M^2, M^4, P^4 and P^6, were constrained according to $M^2 = 0.56M^0$, $M^4 = 0.36M^0$, $P^4 = 0.75P^2$ and $P^6 = 0.50P^2$. The crystal-field Hamiltonian was treated in two different ways in the fitting calculations: (1) no CCF, only the appropriate one-electron crystal-field parameters were used in the calculations; and (2) data fits were performed using the one-electron crystal-field and three CCF parameters.

While introducing the CCF parameters in the fit in the second stage, the ratios of q components of CCF parameters were assigned according to the ratios of q components of B_q^k parameters that were found without CCF parameters. For example, the parameter $G_{10A}^{(4)}$ was assigned to [32]

$$g_{10A}^{(4)} = g_{10AO}^{(4)} + \sum_{Q \neq 0} g_{10AQ}^{(4)}(B_Q^4 / B_0^4). \tag{7}$$

In every fit F^k, ξ and one-electron crystal-field parameters along with CCF parameters were allowed to vary.

All of the empirical energy-level data analysed here were taken directly from the literature [4, 6, 9–11, 16, 47–49] and were used without making any reassignments. The systems examined were NdF$_3$ [6], Nd$_2$Te$_4$O$_{11}$ [16], NdVO$_4$ [11], NdPO$_4$ [11], Nd^{3+}:LiYF$_4$ [21], Nd^{3+}:LaVO$_4$ [11], Nd^{3+}:LaCl$_3$ [10, 47], Nd^{3+}:BaY$_2$F$_8$ [48], Nd^{3+}:YAlO$_3$ [4] and Nd^{3+}:LuAlO$_3$ [4, 9]. The crystal-field symmetries assumed for these systems in the present study are: D$_{3h}$ for Nd^{3+}:LaCl$_3$ [10]; C$_{2v}$ for NdF$_3$ [6], Nd^{3+}:BaY$_2$F$_8$ [48], Nd^{3+}:LaVO$_4$ [11] and NdPO$_4$ [11]; D$_{2d}$ for NdVO$_4$ [11] and Nd^{3+}:LiYF$_4$ [21]; and C$_s$ for Nd$_2$Te$_4$O$_{11}$ [16], Nd^{3+}:YAlO$_3$ [9] and Nd^{3+}:LuAlO$_3$ [9]. However, the exact site symmetry for Nd^{3+}:LaVO$_4$ and NdPO$_4$ is C$_1$ for which 27 different real and imaginary crystal-field parameters are possible, which may not produce consistent parameters for practical purposes.

4. Results and discussions

The atomic and crystal-field parameters of Nd^{3+} ion in 10 systems without and with CCF obtained from the systematic model Hamiltonian and also experimental and calculated energies for some systems are presented in tables 1–5. The parameters under 'No CCF' are obtained without correlation crystal-field parameters in the model Hamiltonian. Similarly under 'CCF' are represented the parameters that are obtained by including CCF parameters in the model Hamiltonian. In the tables, N is the number of energy levels included in the fitting of energy-level calculations, σ denotes the RMS deviation between observed and calculated energies, the numbers shown in parentheses are estimates of the uncertainties in the fitted parameters and the parameters in square brackets were held fixed in the fitting calculations. The results are discussed for each system separately (sections 4.1 to 4.10). The overall results of the parametrization are discussed in sections 4.11 to 4.13.

Table 1. Experimental energies and differences (Δ) between experimental and calculated energies of anomalous $^2H(2)_{11/2}$ multiplet of Nd^{3+} in different systems along with σ values. All values are in cm^{-1}.

System	E_{expt}^a	Δ_B^b	Δ_G^c	System	E_{expt}^a	Δ_B^b	Δ_G^c
NdF_3	16 003	−32	−10	Nd^{3+}:$LaVO_4$	15 924	−17	5
	16 041	−8	0		15 924	−24	−22
	16 057	−2	−4		15 961	−5	8
	16 067	−14	−15		15 989	0	2
	16 111	5	3		16 020	14	1
	16 179	27	2		16 052	20	−3
σ		±18.4	±7.6	σ		±15.74	±9.89
$Nd_2Te_4O_{11}$	15 814	−73	−21	Nd^{3+}:$LaCl_3$	15 906	−19	−10
	15 838	−66	−20		15 948	19	7
	15 891	−18	2		15 922	−15	−5
	15 933	9	5		15 954	0	−2
	15 986	53	10		15 960	1	−13
	16 004	55	8		15 966	−9	−1
σ		±51.5	±13.1	σ		±13.10	±7.62
$NdVO_4$	15 787	−49	−19	Nd^{3+}:BaY_2F_8	15 917	−77	−29
	15 820	−23	−11		15 969	−34	−26
	—	—	—		15 981	−39	−23
	—	—	—		16 055	7	3
	15 866	−7	−31		16 115	53	9
	15 966	77	47		16 155	62	32
σ		±47.19	±30.22	σ		±50.7	±23.0
$LiYF_4$	15 941	−70	−52	Nd^{3+}:$YAlO_3$	15 858	−34	−9
	15 987	−25	−26		15 893	−3	7
	16 013	−18	−14		15 903	−11	−18
	—	—	—		—	—	—
	16 077	4	−5		15 995	12	1
	16 158	58	49		16 095	40	13
σ		±42.67	±34.60	σ		±24.5	±11.0
$NdPO_4$	15 960	−22	—	Nd^{3+}:$LuAlO_3$	15 841	−37	−10
	15 960	−28	—		15 878	−11	1
	15 993	−18	—		15 883	−24	−28
	16 025	−5	—		15 979	21	47
	16 049	3	—		15 988	17	−4
	16 085	23	—		16 071	26	−9
σ		±18.95	—	σ		±23.9	±22.8

[a] Experimental values (E_{expt}) are: NdF_3 [6], $Nd_2Te_4O_{11}$ [16], $NdPO_4$ and $NdVO_4$ [11], $LiYF_4$ [21], $LaVO_4$ [11], $LaCl_3$ [10,47], BaY_2F_8 [48], $YAlO_3$ [4] and $LuAlO_3$ [4,9].
[b] $\Delta_B = E_{expt} − E_{calc}$(No CCF). E_{calc}(No CCF) are obtained from the energy parameters listed under 'No CCF' of NdF_3, BaY_2F_8 and $LaVO_4$ in table 2; $NdVO_4$, $LiYF_4$ and $LaCl_3$ in table 3; $Nd_2Te_4O_{11}$, $YAlO_3$ and $LuAlO_3$ in table 4; and see section 4.4 for $NdPO_4$.
[c] $\Delta_G = E_{expt} − E_{calc}$(CCF). E_{calc}(CCF) are obtained from the energy parameters listed under 'CCF' of NdF_3, BaY_2F_8 and $LaVO_4$ in table 2; $NdVO_4$, $LiYF_4$ and $LaCl_3$ in table 3; $Nd_2Te_4O_{11}$, $YAlO_3$ and $LuAlO_3$ in table 4.

4.1. NdF_3

Caro *et al* [6] reported the analysis of optical absorption spectrum of NdF_3 single crystal at liquid-helium temperature and identified 126 Stark levels. These 126 levels were reanalysed with a uniform model Hamiltonian by Jayasankar *et al* [8] by assuming D_{3h} as well as C_{2v}

Table 2. Atomic, crystal-field and correlation crystal-field parameters for Nd^{3+}:NdF$_3$, Nd^{3+}:BaY$_2$F$_8$ and Nd^{3+}:LaVO$_4$ systems[a]. All values are in cm^{-1}.

Parameter	NdF$_3$		BaY$_2$F$_8$		LaVO$_4$	
	No CCF	CCF	No CCF	CCF	No CCF	CCF
E_{ave}	24 471	24 471(4)	24 336(21)	24 338(8)	24 227(33)	24 223(12)
F^2	72 917	72 923(11)	72 625(80)	72 654(25)	72 120(100)	72 081(38)
F^4	52 674	52 664(17)	53 086(107)	53 068(34)	52 838(157)	52 879(42)
F^6	35 354	35 371(15)	35 425(76)	35 482(30)	35 585(156)	35 536(44)
α	[21.10]	[21.10]	17.23(3.85)	[17.23]	21.18(5)	[21.18]
β	[−594]	[−594]	−513(23)	[−513]	−651(38)	[−651]
γ	[1504]	[1504]	1291(43)	[1291]	1433(74)	[1433]
T^2	[269]	[269]	154(46)	[154]	231(62)	[231]
T^3	[45]	[45]	42(10)	[42]	37(14)	[37]
T^4	[74]	[74]	47(16)	[47]	80(47)	[80]
T^6	[−296]	[−296]	−286(25)	[−286]	−267(30)	[−267]
T^7	[293]	[293]	246(34)	[246]	365(53)	[365]
T^8	[230]	[230]	249(42)	[249]	218(69)	[218]
ξ	883	883(3)	880(10)	880(5)	875(12)	876(5)
M^0	[1.60]	[1.60]	2.43(2.99)	[2.43]	1.49(3)	[1.49]
P^2	[168]	[168]	286(46)	[286]	319(61)	[319]
B_{20}	114	119(12)	−329(40)	−333(31)	−770(29)	−761(23)
B_{22}	−172	−162(11)	410(31)	389(22)	177(30)	203(25)
B_{40}	1192	1219(29)	1672(47)	1615(35)	−733(50)	−689(42)
B_{42}	−125	−120(21)	142(45)	85(36)	874(38)	827(31)
B_{44}	6	−12(20)	−314(41)	−275(33)	224(46)	247(38)
B_{60}	1487	1440(19)	731(43)	763(35)	−677(51)	−658(43)
B_{62}	235	330(22)	427(41)	361(35)	−743(42)	−758(34)
B_{64}	−358	−331(18)	−195(42)	−173(34)	−373(52)	−262(43)
B_{66}	870	878(17)	1029(34)	1037(27)	−313(51)	−324(42)
$G_2^{(4)}$	—	580(103)	—	—	—	—
$G_{10A}^{(4)}$	—	−533(31)	—	−880(51)	—	341(36)
$G_{10B}^{(4)}$	—	−137(34)	—	—	—	—
$G_2^{(4)}/B_{40}$	—	0.48	—	—	—	—
$G_{10A}^{(4)}/B_{40}$	—	−0.44	—	−0.54	—	−0.49
$G_{10B}^{(4)}/B_{40}$	—	−0.11	—	—	—	—
N	126	126	91	91	74	74
σ	±11.39	±10.07	±19.56	±17.12	±17.09	±15.83
S^b	404	406	470	451	420	409

[a] See text (section 2) for definitions of energy parameters. Also see section 4 (first paragraph) for further details of the presentation of the data.
[b] Crystal-field strength parameter, see section 4.12 for details.

crystal-field potential for the $\hat{H}_{CF}$ (equation (3)). In the present work we reanalysed the energy-level data of Caro *et al* [6] and the addition of $G_2^{(4)}$, $G_{10A}^{(4)}$ and $G_{10B}^{(4)}$ parameters in the fit reduces the σ value from 11.39 to 10.07 cm^{-1} for 126 levels (table 2). It is also found that by considering only $G_{10A}^{(4)}$ parameter in the fit the σ value is improved from 11.39 to 10.17 cm^{-1}. Similar results were also obtained for Nd$_2$Te$_4$O$_{11}$ (see section 4.2 and also table 4). Therefore only one CCF parameter ($G_{10A}^{(4)}$) is sufficient to reduce the σ value. The addition of CCF operators in the Hamiltonian resolves the crystal-field splitting problem of ^{2}H(2)$_{11/2}$ multiplet (see table 1) as the σ value has been reduced from 18.4 to 7.6 cm^{-1}. The calculated energy parameters without and with CCF for NdF$_3$ are given in table 2.

Table 3. Atomic, crystal-field and correlation crystal-field parameters for Nd^{3+}:$NdVO_4$, $LiYF_4$ and $LaCl_3$ systems[a]. All values are in cm^{-1}.

Parameter	NdVO₄		LiYF₄		LaCl₃	
	No CCF	CCF	No CCF	CCF	No CCF	CCF
E_{ave}	23 970(11)	23 967(10)	24 419(8)	24 418(8)	24 176(3)	24 176(3)
F^2	71 163(34)	71 137(32)	72 703(24)	72 703(24)	71 892(9)	71 893(8)
F^4	51 591(41)	51 620(39)	52 340(39)	52 337(39)	52 219(14)	52 218(13)
F^6	35 318(40)	35 270(38)	35 795(32)	35 787(32)	35 489(11)	35 489(11)
α	[16.50]	[16.50]	[22.10]	[22.10]	[22.12]	[22.12]
β	[−548]	[−548]	[−574]	[−574]	[−656]	[−656]
γ	[1485]	[1485]	[1482]	[1482]	[1583]	[1583]
T^2	[303]	[303]	[350]	[350]	[372]	[372]
T^3	[31]	[31]	[46]	[46]	[40]	[40]
T^4	[103]	[103]	[87]	[87]	[61]	[61]
T^6	[−245]	[−245]	[−299]	[−299]	[−291]	[−291]
T^7	[297]	[297]	[368]	[368]	[347]	[347]
T^8	[300]	[300]	[320]	[320]	[355]	[355]
ξ	869(5)	870(5)	871(6)	871(6)	879(2)	879(2)
M^0	[0.95]	[0.95]	[0.14]	[0.14]	[1.84]	[1.84]
P^2	[133]	[133]	[84]	[84]	[281]	[281]
B_{20}	−40(30)	−10(28)	379(23)	371(23)	153(8)	153(7)
B_{40}	359(43)	372(39)	−957(43)	−948(42)	−345(14)	−325(13)
B_{44}	1144(27)	1 104(26)	−1206(31)	1192(31)	—	—
B_{60}	−1071(38)	−1031(36)	44(39)	39(38)	−722(14)	−722(13)
B_{64}	82(37)	102(35)	−1078(31)	−1079(31)	—	—
B_{66}	—	—	—	—	475(13)	471(12)
$G^{(4)}_{10A}$	—	−177(23)	—	140(45)	—	217(21)
$G^{(4)}_{10A}/B_{40}$	—	−0.48	—	−0.15	—	−0.67
N	71	71	129	129	128	128
σ	±18.40	±17.07	±24.13	±23.79	±8.91	±8.29
S	363	351	459	456	176	174

[a] See footnotes to table 2.

4.2. Nd₂Te₄O₁₁

Absorption measurements at liquid-helium temperature have been performed on the monoclinic $Nd_2Te_4O_{11}$ by Cascales et al [16]. Crystal-field level analyses have also been carried out by assuming the approximate (effective) C_{2v} as well as C_s site symmetry instead of the actual C_1 site symmetry for Nd. Considering 103 crystal-field levels, the fit gave the σ value of 25.8 cm^{-1} for C_{2v} site symmetry approximation and 22.7 cm^{-1} for C_s site symmetry approximation. In order to reduce the σ value for the abnormal $^2H(2)_{11/2}$ multiplet, they modified the reduced matrix element, reducing by a factor of 4 ($U^4/4$), and obtained the σ value of 21.8 and 17.8 cm^{-1} for C_{2v} and C_s site symmetries, respectively. The present analysis with uniform free-ion terms in $\hat{H}_A$ and also without and with CCF parameters in model Hamiltonian yields improved σ value for 103 levels of $Nd_2Te_4O_{11}$. By adding CCF we are able to reduce the σ value from 17.7 to 12.73 cm^{-1} for 103 levels (table 4). The inclusion of CCF in the fit reduces the σ value not only for the anomalous $^2H(2)_{11/2}$ multiplet but also for other levels. The σ value for $^2H(2)_{11/2}$ has been reduced from 51.5 to 13.1 cm^{-1} (see table 1). It is noticed from NdF_3 (table 2) and $Nd_2Te_4O_{11}$ (table 4) CCF analyses that $G^{(4)}_{10A}$ parameter is more effective than the other two possible $G^{(4)}_2$ and $G^{(4)}_{10B}$ parameters [32, 35].

Table 4. Atomic, crystal-field and correlation crystal-field parameters of Nd^{3+} in $Nd_2Te_4O_{11}$, $YAlO_3$ and $LuAlO_3$[a]. All values are in cm^{-1}.

Parameter	$Nd_2Te_4O_{11}$		$YAlO_3$		$LuAlO_3$	
	No CCF	CCF	No CCF	CCF	No CCF	CCF
E_{ave}	24 073(9)	24 073(7)	24 120(8)	24 118(8)	24 019(28)	24 018(6)
F^2	70 858(30)	70 853(22)	70 837(120)	70 826(25)	70 158(106)	70 152(19)
F^4	52 870(36)	52 874(27)	50 815(151)	50 826(28)	51 629(129)	51 647(23)
F^6	37 757(35)	37 734(26)	35 331(172)	35 307(29)	35 056(144)	35 042(23)
α	[21.75]	[21.75]	23.15(5.00)	[23.15]	21.02(2.33)	[21.02]
β	[−654]	[−654]	−684(34)	[−684]	−638(15)	[−638]
γ	[1033]	[1033]	1690(91)	[1690]	1542(77)	[1542]
T^2	[749]	[749]	501(69)	[501]	489(56)	[489]
T^3	[30]	[30]	37(14)	[37]	37(8)	[37]
T^4	[85]	[85]	56(48)	[56]	67(10)	[67]
T^6	[−326]	[−326]	−298(29)	[−298]	−321(23)	[−321]
T^7	[491]	[491]	251(42)	[251]	396(37)	[396]
T^8	[683]	[683]	511(74)	[511]	431(53)	[431]
ξ	871(4)	871(3)	876(8)	876(3)	875(6)	875(3)
M^0	[0.75]	[0.75]	1.84(2.30)	[1.84]	1.72(2.00)	[1.72]
P^2	[181]	[181]	158(36)	[158]	182(29)	[182]
B_{20}	359(27)	345(22)	34(32)	35(27)	−221(27)	−233(22)
B_{22}	−199(24)	−195(19)	572(20)	569(16)	629(18)	611(14)
B_{40}	1102(40)	1263(40)	−659(41)	−618(32)	−372(35)	−314(28)
B_{42}	534(50)	488(40)	1045(32)	988(27)	1058(26)	964(22)
$I B_{42}$	751(53)	723(35)	−314(46)	−368(37)	60(36)	250(28)
B_{44}	237(42)	175(36)	−71(41)	−43(33)	−346(37)	−334(29)
$I B_{44}$	106(51)	196(35)	458(35)	422(27)	588(35)	663(27)
B_{60}	100(48)	51(33)	−809(47)	−870(37)	−708(44)	−1094(30)
B_{62}	126(48)	159(39)	532(39)	524(31)	558(33)	565(24)
$I B_{62}$	−91(45)	−85(32)	−235(42)	268(33)	−105(44)	75(33)
B_{64}	−526(50)	−547(35)	1207(51)	1078(45)	1483(28)	1199(32)
$I B_{64}$	316(69)	143(50)	−869(62)	−1006(48)	214(57)	700(40)
B_{66}	−246(42)	−324(37)	319(47)	372(36)	−201(36)	−271(28)
$I B_{66}$	10(62)	−2(47)	343(44)	292(36)	320(41)	−47(29)
$G_2^{(4)}$	—	501(35)	—	—	—	—
$G_{10A}^{(4)}$	—	−555(40)	—	301(26)	—	214(17)
$G_{10B}^{(4)}$	—	−590(47)	—	—	—	—
$G_2^{(4)}/B_{40}$	—	0.40	—	—	—	—
$G_{10A}^{(4)}/B_{40}$	—	−0.44	—	−0.49	—	−0.68
$G_{10B}^{(4)}/B_{40}$	—	−0.47	—	—	—	—
N	103	103	96	96	106	106
σ	±17.70	±12.73	±13.74	±11.97	±12.97	±10.87
S	388	396	568	577	575	578

[a] See footnotes to table 2.

4.3. NdVO₄

The absorption spectra of neat $NdVO_4$ were carried out at 300, 77 and 4.2 K and 71 crystal-field levels were identified [11]. The energy levels were analysed by assuming D_{2d} site symmetry with an RMS deviation of 19.4 cm^{-1} for 71 levels. The present crystal-field analysis yields 18.4 and 17.07 cm^{-1} without and with CCF parameter respectively. Only $G_{10A}^{(4)}$ parameter along with other parameter values are given in table 3. The inclusion of $G_2^{(4)}$ and $G_{10B}^{(4)}$ parameters did not show any improvement in the fit as noticed in the analyses of NdF_3 and $Nd_2Te_4O_{11}$ systems and also in [32].

4.4. NdPO$_4$

Antic-Fidancev *et al* [11] reported the spectroscopic data for NdPO$_4$ from absorption studies. The crystal-field analysis was carried out by assuming the effective C$_{2v}$ site symmetry instead of the exact C$_1$ site symmetry and an RMS deviation of 18.3 cm^{-1} for 90 crystal-field levels obtained. The present crystal-field analysis (with C$_{2v}$ symmetry) has improved the σ value from 18.3 cm^{-1} [11] to 16.67 cm^{-1} for 90 crystal-field levels and the resulting parameters (in cm^{-1}) are $E_{ave} = 24\,207(31)$, $F^2 = 70\,850(109)$, $F^4 = 50\,572(171)$, $F^6 = 33\,503(178)$, $\alpha = 21.35(3)$, $\beta = -606(19)$, $\gamma = 2120(100)$, $T^2 = 504(43)$, $T^3 = 26(9)$, $T^4 = 74(11)$, $T^6 = -334(23)$, $T^7 = 433(30)$, $T^8 = 436(44)$, $\xi = 879(6)$, $M^0 = [1.84]$, $P^2 = [281]$, $B_{20} = -618(23)$, $B_{22} = 103(22)$, $B_{40} = -785(37)$, $B_{42} = 233(37)$, $B_{44} = 728(32)$, $B_{60} = -1078(49)$, $B_{62} = 850(40)$, $B_{64} = -305(44)$ and $B_{66} = -67(41)$. Each of the CCF parameters $G_2^{(4)}$, $G_{10A}^{(4)}$ and $G_{10B}^{(4)}$ were added to the fit with incredible success in solving the crystal-field splitting problems for the energy-level structure of NdPO$_4$. However, the σ value for the abnormal ^{2}H(2)$_{11/2}$ multiplet is only 18.95 cm^{-1} without CCF parametrization (table 1).

4.5. Nd^{3+}:LiYF$_4$

Empirical energy-level data for Nd^{3+}:LiYF$_4$ were taken from a study reported by da Gamma *et al* [49]. These data were fitted using a crystal-field Hamiltonian of D$_{2d}$ symmetry (which is an approximation of the actual S$_4$ site symmetry of the Nd^{3+} ions in this system). The energy parameters obtained without and with CCF are given in table 3. The present CCF analysis is slightly different from the CCF analysis of Li and Reid [32] since our data set ($N = 129$) is different from Li and Reid's data set ($N = 121$). The present atomic and crystal-field parameters (without CCF) are in agreement with the earlier analysis [29].

4.6. Nd^{3+}:LaVO$_4$

The electronic spectrum of Nd^{3+}:LaVO$_4$ has been studied along with the crystal-field analysis for the 74 observed crystal-field levels with RMS deviation of 20.1 cm^{-1} by assuming C$_{2v}$ site symmetry [11]. The new crystal-field analysis without and with CCF parameters in the model Hamiltonian by assuming C$_{2v}$ site symmetry for Nd^{3+}:LaVO$_4$ is shown in table 2. By adding $G_{10A}^{(4)}$ parameter in the CCF analysis we obtained a satisfactory fit for all the levels along with the improved σ value for ^{2}H(2)$_{11/2}$ level. Addition of $G_{10A}^{(4)}$ parameter in the fit improves the σ value from 17.09 to 15.83 cm^{-1} for 74 crystal-field levels. The effect of other CCF parameters $G_{10B}^{(4)}$ and $G_2^{(4)}$ on the fit is not of much significance.

4.7. Nd^{3+}:LaCl$_3$

The energy-level analysis of neodymium chloride in LaCl$_3$ host has been widely studied and quantum-number assignments were made for all the observed levels. The recent study includes photoexcited Nd^{3+} ion in LaCl$_3$ by Pelletier-Allard *et al* [10] and pressure effects on crystal-field levels by Jayasankar *et al* [50]. The present analysis is similar to 128 levels at 0 GPa by Jayasankar *et al* [50] and slightly different from the Li and Reid [32] analysis. Li and Reid's analysis involves only 87 energy-level data of Crosswhite *et al* [51]. We have carried out fits using the extensive data set of Pelletier-Allard *et al* [10], where 127 energy levels were reported, plus one ^{2}H(2)$_{11/2}$ level from Troster *et al* [47], making a total of 128 Stark levels. The energy parameters obtained in the fit without and with CCF are given in table 3. The anomalous (^{2}H(2)$_{11/2}$) multiplet of Nd^{3+}:LaCl$_3$ in different parametrizations is shown in table 1.

Table 5. Experimental energies and differences (Δ) between experimental and calculated energies of Nd^{3+} in BaY_2F_8 and $YAlO_3$ systems along with σ values for individual multiplets[a,b]. All values are in cm^{-1}.

Level	BaY_2F_R			$YAlO_3$		
	E_{expt}	Δ_B	Δ_G	E_{expt}	Δ_B	Δ_G
$^4I_{9/2}$	0	−27	−30	0	−7	−9
	93	7	3	118	−28	−23
	179	15	16	212	−7	−8
	283	−24	−16	500	7	8
	546	−15	−15	671	−10	−8
σ		±18.7	±18.3		±14.4	±12.2
$^4I_{11/2}$	1991	5	5	2023	9	7
	2025	3	0	2097	5	3
	2065	−2	−1	2158	−11	−10
	2102	21	26	2264	7	10
	2228	−12	−11	2323	−5	−4
	2296	24	27	2378	−3	−1
σ		±14.2	±16.2		±7.2	±6.8
$^4I_{13/2}$	3935	−1	−3	3953	17	15
	3975	10	7	4021	23	20
	3991	−14	−13	4092	−10	−10
	4052	27	28	4200	14	19
	4202	9	12	4291	23	26
	4252	7	10	4328	−5	−4
	4287	5	9	4446	2	3
σ		±12.9	±13.8		±15.5	±15.7
$^4I_{15/2}$	5829	−18	−16	5757	6	6
	5888	12	8	5893	7	5
	5948	−19	−26	6011	−26	−26
	6048	−4	0	6240	15	19
	6295	−7	−9	6307	−9	−7
	6355	0	7	6402	12	15
	6437	13	18	6687	−2	−2
	6498	−22	−14	6743	−24	−27
σ		±13.9	±14.6		±15.0	±16.3
$^4F_{3/2}$	11 519	1	1	11 421	−4	−6
	11 611	−2	−2	11 550	13	3
σ		±2.0	±2.0		±8.2	±14.2
$^4F_{5/2}$	12 516	−7	−25	12 411	13	3
	12 538	−9	−12	12 447	1	16
	12 623	33	45	12 511	14	−7
σ		±20.0	±30.6		±11.2	±10.4
$^2H_{9/2}$	12 655	20	0	12 561	−9	−2
	12 671	−17	1	12 593	−10	−10
	12 726	−18	9	12 713	−11	0
	12 812	2	9	12 742	−19	2
	12 857	−2	−32	12 883	18	1
σ		±14.5	±15.9		±14.3	±4.7

Table 5. (continued)

$^4F_{7/2}$	13461	−4	−6	13323	−4	−4
	13549	12	17	13452	−9	−7
	13633	12	13	13607	1	1
	13671	−37	−30	13651	6	6
σ		±20.5	±18.7		±5.8	±5.0
$^4S_{3/2}$	13652	0	0	13565	−5	−8
	13659	1	1	13589	7	5
σ		±0.7	±0.7		±6.1	±6.7
$^4F_{9/2}$	14732	−5	4	14665	−5	−1
	14793	18	21	14723	−5	−2
	14848	−1	−2	14740	−16	−15
	14899	−18	−25	14793	−13	−20
	14970	32	31	14928	27	25
σ		±18.5	±20.3		±15.6	±15.2
$^2H_{11/2}$	15917	−77	−29	15858	−34	−9
	15969	−34	−26	15893	−3	7
	15981	−39	−23	15903	−11	−18
	16055	7	3	—	—	—
	16115	53	9	15995	12	1
	16155	62	32	16095	40	13
σ		±50.7	±23.0		±24.5	±11.0
$^4G_{5/2'}$	17156	10	2	16963	1	−4
$^2G_{7/2}$	17225	−11	−7	17023	3	−1
	17301	−4	4	17116	0	2
	17425	−1	−1	17295	20	16
	17449	−13	−11	17313	−16	−13
	—	—	—	17364	9	10
	—	—	—	17456	−2	9
σ		±9.1	±6.1		±10.36	±9.46
$^4G_{7/2}$	19026	18	20	18846	12	5
	19095	17	19	18893	−5	−5
	19142	−10	5	18975	−2	6
	19212*	—	—	19077	−23	−13
σ		±15.6	±16.1		±13.1	±7.7
$^2K_{13/2'}$	—	—	—	19245	−5	−7
$^4G_{9/2}$	19440	9	−4	19309	17	15
	—	—	—	19350	−16	−17
	—	—	—	19425	2	3
	19564	−2	−7	19546	24	25
	19594	7	−1	19806	35	28
	19627	−9	−3	19873	−3	−10
	19685	−21	−29	19924	−25	−21
	19716	−9	−10	—	—	—
	19763	−1	−1	—	—	—
	20113*	—	—	—	—	—
σ		±10.3	±12.1		±19.4	±17.3
$^2G_{9/2}$	21039*	—	—	20865	9	6
	21026	14	12	20894	7	5

Table 5. (continued)

	21 077	16	19	20 955	−16	−11
	21 113	−1	19	21 041	7	13
	—	—	—	21 110	0	4
σ		±12.3	±17.0		±9.3	±8.6
$^2D_{3/2}$	21 211	−5	2	—	—	—
	21 248	3	9	—	—	—
σ		±4.1	±6.5	—	—	—
$^4G_{11/2'}$	21 338	−25	−33	21 231	17	13
$^2K_{15/2}$	21 395	−22	−26	21 276	−6	−9
	21 478	27	20	21 294	−14	−13
	21 510	−17	−21	21 367	−13	−16
	21 744	28	21	21 464	−1	3
	21 786	12	19	21 536	13	13
	—	—	—	21 580	6	9
	21 911*	—	—	21 630	−1	−1
	21 988*	—	—	21 654	−8	−7
	22 080*	—	—	21 718	8	14
	—	—	—	21 748	1	0
	—	—	—	21 834	−10	−11
	—	—	—	21 906	8	1
	—	—	—	21 930	−5	−4
σ		±17.9	±19.7		±9.7	±9.0
$^2P_{1/2}$	23 392	3	0	23 164	−1	3
σ		±3.0	0.0		±1.0	±3.0
$^2D_{5/2}$	23 838	1	0	23 463	−27	−24
	—	—	—	23 635	13	11
	—	—	—	23 759	14	16
σ		±1.0	0.0		±19.1	±17.7
$^2P_{3/2}$	26 241	7	−1	25 981	1	4
	26 340	−4	−8	26 123	5	10
σ		±5.4	±5.7		±3.8	±7.4
$^4D_{3/2}$	28 086	17	18	—	—	—
	28 185	−29	−31	—	—	—
σ		±23.9	±25.6		—	—
$^4D_{5/2}$	28 393	6	10	—	—	—
	28 531*	—	—	—	—	—
	28 629	8	35	—	—	—
σ		±20.6	±25.5	—	—	—
$^2F_{5/2}$	38 437	−12	−9	—	—	—
σ		±12.0	±9.0	—	—	—
$^2F_{7/2}$	39 932	12	15	—	—	—
σ		±12.0	±15.0	—	—	—

[a] The levels marked with a star are not used in the fit.
[b] See footnotes to table 1 related to BaY_2F_8 and $YAlO_3$.

4.8. $Nd^{3+}:BaY_2F_8$

Locations and assignments of 103 crystal-field levels of $Nd^{3+}:BaY_2F_8$ have been reported by Joubert *et al* [48] from absorption and fluorescence measurements at low temperature (helium refrigerator temperature). We carried out energy level calculations using an approximate model Hamiltonian with C_{2v} site symmetry instead of the actual C_2 site symmetry [48]. The fit includes only 91 levels out of 103 levels reported. The levels omitted in the fit are shown with a star as they differ considerably from calculated values (table 5). Experimental energies and differences between experimental and calculated energies of $Nd^{3+}:BaY_2F_8$ are given in table 5. Without CCF, the σ value is 19.56 cm^{-1} for 91 levels. With the inclusion of CCF, the σ value has been reduced from 19.56 to 17.12 cm^{-1} for 91 levels (table 2). With CCF parameters, the σ value for $^2H(2)_{11/2}$ has been reduced from 50.7 to 23.0 cm^{-1} (table 1).

4.9. $Nd^{3+}:YAlO_3$

The interest in yttrium orthoaluminate (YAlO$_3$) as a laser host material has spanned a sequence of papers reporting optical spectra [4], crystal-field splitting analysis [5, 7], luminescence properties [4], etc. [4, 5, 7, 52]. Even though a number of papers have appeared on crystal-field analysis of $Nd^{3+}:YAlO_3$, there is no correlation between one set of energy parameters and another set of parameters, mainly due to differences in calculations as well as differences in the definitions of model Hamiltonian. For example, the parameter values obtained for $Nd^{3+}:YAlO_3$ by Karayianis *et al* [5], Deb [7] and Faucher *et al* [52] are different from one another.

   We carried out the crystal-field analysis for $Nd^{3+}:YAlO_3$ without and with CCF parameters in the model Hamiltonian. The point-group symmetry for Nd^{3+} at the yttrium site is C_s (C_{1h}). Thus, for C_s site symmetry, 14 independent crystal-field parameters are used to predict crystal-field splittings besides one CCF parameter. The experimental energy levels are taken from Kaminskii [4]. Tables 4 and 5 show the energy parameters and experimental energies and differences between experimental and calculated energy levels respectively for $Nd^{3+}:YAlO_3$. The σ value is 13.74 cm^{-1} for 96 levels and reduces to 11.97 cm^{-1} when CCF is added in the model Hamiltonian.

4.10. $Nd^{3+}:LuAlO_3$

So far the reported work on the crystal-field analysis of $Nd^{3+}:LuAlO_3$ is restricted to one-electron crystal-field parameters only [9]. It should be pointed out that, owing to the large number of crystal-field parameters for C_s point symmetry group [9], there might exist different sets of crystal-field parameters yielding results with more or less similar quality. The present crystal-field analysis was carried out on empirical data reported by Faucher *et al* [9] and Kaminskii [4]. For 106 Stark levels, the σ value is 12.97 cm^{-1} without CCF parameters. By adding $G_{10A}^{(4)}$ parameter, the value of σ is reduced to 10.87 cm^{-1}. The phenomenological parameters for $Nd^{3+}:LuAlO_3$ shown in table 4 are more refined and accurate than the parameters reported by Faucher *et al* [9]. However, the present set of parameters also differs from *ab initio* calculations [9] and are close to the real part of the one-electron crystal-field parameters of Faucher *et al* [9].

4.11. Data fits, energy parameters and ab initio calculations

The parameters obtained by varying the atomic and crystal-field parameters to minimize the deviation σ for the energy levels of Nd^{3+} in 10 different hosts (or compounds), are

summarized in tables 2–4. The number of energy levels used in the fit varies from $N = 129$ (Nd^{3+}:$LiYF_4$) to $N = 71$ (Nd^{3+}:$NdVO_4$). Relatively large numbers of levels are used for Nd^{3+}:$LiYF_4$ ($N = 129$), Nd^{3+}:$LaCl_3$ ($N = 128$) and Nd^{3+}:NdF_3 ($N = 126$) out of 182 possible levels for $4f^3$ configuration of Nd^{3+}. The smallest data set used is $N = 71$ for Nd^{3+}:$NdVO_4$.

Comparison of the crystal-field parameters obtained without and with the inclusion of CCF terms in $\hat{H}$ are listed under 'No CCF' and 'CCF' columns respectively in tables 2–4. The standard deviation without CCF lies between 8.91 (Nd^{3+}:$LaCl_3$) and 24.13 cm^{-1} (Nd^{3+}:$LiYF_4$). Out of 10 data sets examined, the Nd^{3+}:$LaCl_3$ fit is very good since the σ value is 8.91 cm^{-1} for $N = 128$ levels with only four one-electron crystal-field parameters. In each system, inclusion of the CCF terms in the crystal-field Hamiltonian produces lower σ values (except for Nd^{3+}:$NdPO_4$). By adding CCF parameters in the $\hat{H}$, the greatest influence is found for Nd^{3+}:$Nd_2Te_4O_{11}$ system as the σ value is reduced from 17.7 to 12.73 cm^{-1} for 103 crystal-field levels.

In table 1 the energy-level splitting of the anomalous $^2H(2)_{11/2}$ multiplet fit is tabulated without and with CCF. As seen from table 1, in particular for Nd^{3+}:$Nd_2Te_4O_{11}$ and Nd^{3+}:BaY_2F_8 systems, the $^2H(2)_{11/2}$ multiplet yields a poor fit with one-electron crystal-field parameters. By adding CCF parameters in the fit the σ value for this multiplet is reduced from 51.5 to 13.1 cm^{-1} and from 50.7 to 23.0 cm^{-1} for Nd^{3+}:$Nd_2Te_4O_{11}$ and BaY_2F_8 systems, respectively. A similar decreasing trend in the σ value of the anomalous $^2H(2)_{11/2}$ multiplet is noticed for other systems also.

Comparing the parameter sets that are obtained without and with CCF terms in $\hat{H}$, we note that both the atomic and one-electron crystal-field parameters (B_{kq}) are not significantly different when CCF is introduced in $\hat{H}$. Identifying trends in the values of free-ion parameters (tables 2–4) is often difficult because smooth progressions are not always observed among changing coordination environments for a particular lanthanide ion. This may be due to the fact that the number of levels, N, used in the fit differs from one system to another.

Detailed *ab initio* calculations of CCF effects for the simple Pr^{3+}–Cl^- system have been carried out by Ng and Newman [37]. If the predicted ratios for $G_2^{(4)}/B_{40}$, $G_{10A}^{(4)}/B_{40}$ and $G_{10B}^{(4)}/B_{40}$ are examined, we find that there is consistency between *ab initio* calculations and the phenomenological parameters. The ratios predicted for $G_2^{(4)}/B_{40}$, $G_{10A}^{(4)}/B_{40}$ and $G_{10B}^{(4)}/B_{40}$ are 0.29, -0.50 and -0.15 respectively. We obtained the ratios as 0.48, -0.44 and -0.11 for Nd^{3+}:NdF_3 (table 2) and 0.40, -0.44 and -0.47 for Nd^{3+}:$Nd_2Te_4O_{11}$ (table 4). The predicted ratio from *ab initio* calculations for $G_{10A}^{(4)}/B_{40}$ is -0.50, which is consistent with our phenomenological results of -0.54 (Nd^{3+}:BaY_2F_8), -0.49 (Nd^{3+}:$YAlO_3$), -0.68 (Nd^{3+}:$LuAlO_3$), -0.48 (Nd^{3+}:$NdVO_4$), -0.49 (Nd^{3+}:$LaVO_4$), -0.67 (Nd^{3+}:$LaCl_3$) and -0.15 (Nd^{3+}:$LiYF_4$). These results are in agreement with CCF analysis of other lanthanides [31–35].

4.12. Crystal-field strength

In order to acquire information about the strength (S) of the crystal-field effect experienced by the Nd^{3+} ion in different compounds, we have used the relationship defined by Chang *et al* [53]

$$S = \left[\frac{1}{3} \sum_k \left(\frac{1}{2k+1} \right) \left(B_{k0}^2 + 2 \sum_{m>0} (R B_{km}^2 + I B_{km}^2) \right) \right]^{1/2}. \qquad (8)$$

Equation (8) provides a means of comparing the crystal-field strengths of different compounds on Nd^{3+} ion. The resulting values, S, obtained with the crystal-field parameters

are listed in tables 2–4. The order of magnitude (cm^{-1}) of S without CCF follows the trend:

$$575(\text{LuAlO}_3) > 568(\text{YAlO}_3) > 470(\text{BaY}_2\text{F}_8) > 459(\text{LiYF}_4) > 420(\text{LaVO}_4)$$

$$> 406(\text{NdPO}_4) > 404(\text{NdF}_3) > 388(\text{Nd}_2\text{Te}_4\text{O}_{11}) > 363(\text{NdVO}_4)$$

$$> 176(\text{LaCl}_3).$$

Nd^{3+} ion experiences relatively stronger crystal-field strength in LuAlO_3 and weaker crystal-field strength in LaCl_3 environment compared to the remaining systems. We noticed a similar trend of S parameter when CCF operators were added in Hamiltonian H.

4.13.   Comparison between CCF analysis and matrix element modification to improve anomalous $^2H(2)_{11/2}$ multiplet

Our parametric fits to improve the anomalous crystal-field splitting of $^2H(2)_{11/2}$ multiplet of Nd^{3+} are far better than the procedure adopted by Cascales *et al* [16] and Faucher *et al* [21]. In table 6, we compare the $^2H(2)_{11/2}$ fit from the present analysis with that of [16] for $\text{Nd}^{3+}:\text{Nd}_2\text{Te}_4\text{O}_{11}$. The σ value with CCF parameter for $^2H(2)_{11/2}$ has improved from 51.5 to 13.1 cm^{-1} and is better than the reported value from matrix element modification (σ is improved from 52.4 to 13.5 cm^{-1}). The matrix element modification proposed in [16] and [21] for $^2H(2)_{11/2}$ multiplet, $(^2H(2)_{11/2}\|U^\lambda\|^2H(2)_{11/2})$ reduced by 4, yields an improved fit only for $^2H(2)_{11/2}$ multiplet without affecting other levels and also without changing crystal-field parameter values. The adjustment of matrix element is somewhat arbitrary (only a mathematical trick), which was difficult to explain physically. Our approach has the advantage of comparing the phenomenological CCF parameters with the *ab initio* calculations.

Table 6. Energy levels for the $^2H(2)_{11/2}$ multiplet of $\text{Nd}^{3+}:\text{Nd}_2\text{Te}_4\text{O}_{11}$ computed without and with CCF operators and comparison with the matrix element modification (in C_s site symmetry). All values are in cm^{-1}.

	Present[a]				Reported[b]			
E_{expt}	E_{calc} (No CCF)	Δ_B	E_{calc} (CCF)	Δ_G	E_{calc}	Δ	E_{calc}	Δ
15 814	15 887	−73	15 859	−21	15 888	−74	15 836	−22
15 838	15 904	−66	15 864	−20	15 905	−67	15 862	−24
15 891	15 909	−18	15 889	2	15 911	−20	15 886	5
15 933	15 924	9	15 928	5	15 925	8	15 933	0
15 986	15 933	53	15 976	10	15 931	55	15 988	−2
16 004	15 949	55	15 996	8	15 949	55	16 007	−3
$\sigma(^2H(2)_{11/2})$		±51.5		±13.1		±52.4		±13.5
σ(overall)		±17.7		±12.73		±22.7		±17.8

[a] See table 1 (related to $\text{Nd}_2\text{Te}_4\text{O}_{11}$) and sections 4.2 and 4.13 for details.
[b] See table 3 of Cascales *et al* [16] for details.

5. Conclusions

We carried out the problem of parametrizing correlation effects in the crystal-field splittings of the $4f^3$ configuration of Nd^{3+} in 10 crystal systems. The results presented here indicate

that the CCF effects for Nd^{3+} ion resolve not only the anomalous $^2H(2)_{11/2}$ multiplet fitting but also improve the overall RMS deviation. All features related to crystal-field level fits have been reinvestigated systematically with a uniform model Hamiltonian, and the overall crystal-field level parametrization of the experimental energy-level data is reasonably good. It is interesting to note that the predicted ratio from *ab initio* calculation for $G_{iQ}^{(4)}/B_{40}$ of Pr^{3+}:$PrCl_3$ is consistent with our phenomenological results of Nd^{3+} ion and also in agreement with CCF analysis of other lanthanides and actinides.

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