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Spin-correlated Crystal-field Interactions in NdF_3, Nd^{3+}:LaF_3, and Nd^{3+}:$LiYF_4$*

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Locations and assignments for a reasonably large number of crystal-field energy levels have been reported for Nd^{3+} in NdF_3 [1], LaF_3 [2] and $LiYF_4$ [3]. These data have been analysed in terms of parametrized Hamiltonians for the $4f^3$ electronic configuration of Nd^{3+} in the appropriate crystal-field symmetries (actual or effective). However, the extant analyses differ with respect to the number of parameters used to fit the empirical energy level data, and in each case the crystal-field Hamiltonian was restricted to *one-electron* interaction operators. In the study reported here, we re-analysed the energy level data available for NdF_3 [1], Nd^{3+}:LaF_3 [2], and Nd^{3+}:$LiYF_4$ [3], using model Hamiltonians that are commensurate with respect to their 'free-ion' parametrizations and which include at least partial consideration of *two-electron* crystal-field interactions. The results obtained from these analyses provide a better basis for comparing the Hamiltonian parameters (and their underlying physical interactions) for the respective systems, and they afford an assessment of *spin-correlated crystal-field* (SCCF) effects in these systems.

As defined here, SCCF effects derive from spin-correlated two-electron crystal-field interactions, and they represent a part of the general (many-electron) correlation crystal field [4–7]. They are included in our parametrized crystal-field Hamiltonian according to:

$$\mathcal{H}_{CF} = \sum_{k,q} \sum_{i} [B^k_q u^k_q(i) + b^k_q \boldsymbol{S}\cdot \boldsymbol{s}_i u^k_q(i)] \qquad (1)$$

where i labels the 4f electrons; $u^k_q(i)$ is a one-electron unit-tensor operator; $\boldsymbol{S}$ and $\boldsymbol{s}_i$ are total spin and one-electron spin operators, respectively; and B^k_q and b^k_q are the one-electron and spin-correlated crystal-field parameters, respectively. This parametrization of the crystal-field Hamiltonian to include SCCF effects conforms to that used previously by Newman and coworkers [5–7].

Calculations

All energy level calculations were carried out using the complete $SLJM_J$ basis set for the $4f^3$ electronic configuration of Nd^{3+}. In each case, the isotropic ('free-ion') part of the Hamiltonian contained 20 parameters: E_{ave}, F^k ($k = 2, 4, 6$), α, β, γ, T^i ($i = 2, 3, 4, 6, 7, 8$), ζ_{so}, M^k ($k = 0, 2, 4$), and P^k ($k = 2, 4, 6$), where the notation and definitions for these parameters follow the usual conventions [2, 8, 9], except that the spin–spin parts of the operators associated with the M^k parameters were omitted in the present study. All but four of these parameters were allowed to freely vary in performing fits of calculated-to-experimental energy level data. The parameters not varied independently were M^2, M^4, P^4 and P^6. These parameters were constrained according to the relationships: $M^2 = 0.56M^0$, $M^4 = 0.38M^0$, $P^4 = 0.75P^2$, and $P^6 = 0.50P^2$.

The empirical data analysed here have been reported elsewhere [1–3]. For NdF_3, we used the 127 energy levels located and assigned by Caro *et al.* [1], and for Nd^{3+}:LaF_3, we used the 139 levels reported by Carnall *et al.* [2]. For each of these systems, we carried out two different crystal-field analyses: one in which the $\mathcal{H}_{CF}$ operator was defined to have exact D_{3h} symmetry, and one in which the $\mathcal{H}_{CF}$ operator has C_{2v} symmetry. A description and rationale of the latter have been given previously [1]. The actual site symmetry of the Nd^{3+} ions is C_2 [10, 11], but the 'effective' crystal-field potential for the 4f electrons appears to have near-D_{3h} symmetry. For both our D_{3h} and C_{2v} Hamiltonians, the axis of quantization was chosen to be parallel to the crystallographic *c*-axis and coincident with the C_3 symmetry axis of D_{3h}. This is not a symmetry axis in the C_{2v} point group.

Empirical energy level data for Nd^{3+}:$LiYF_4$ were taken from a study reported by da Gama *et al.* [3]. These data were fitted using a crystal-field Hamiltonian of D_{2d} symmetry (which is an approximation to the actual S_4 site symmetry of the Nd^{3+} ions in this system).

Results and Discussion

Parameter values obtained from our calculated *versus* experimental energy level fits are listed in Tables I–III along with the σ values for these fits. In

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TABLE I. Energy Parameters for Nd^{3+} in NdF_3 and LaF_3 (D_{3h} Crystal-field Hamiltonian)[a]

Parameter[b]	Without SCCF		With SCCF	
	NdF_3	Nd^{3+}:LaF_3	NdF_3[d]	Nd^{3+}:LaF_3
E_{ave}	24471(17)	24480(6)	24471(5)	24479(6)
F^2	72917(61)	73006(19)	[72917]	72993(19)
F^4	52674(97)	52699(43)	[52674]	52705(42)
F^6	35354(102)	35775(29)	[35354]	35753(28)
α	21.1(2.1)	21.5 (1.6)	[21.1]	21.5(1.6)
β	−594(16)	−591(12)	[−594]	−593(12)
γ	1504(56)	1451(18)	[1504]	1457(17)
T^2	269(25)	318(11)	[269]	317(11)
T^3	45(10)	36(7)	[45]	35(7)
T^4	74(11)	55(9)	[74]	53(8)
T^6	−296(14)	−282(11)	[−296]	−281(11)
T^7	293(20)	322(13)	[293]	323(13)
T^8	230(23)	302(14)	[230]	312(14)
ζ_{so}	883(7)	886(5)	[883]	886(5)
M^0	1.6(2.2)	2.4(1.6)	[1.6]	2.4(1.6)
P^2	168(33)	208(25)	[168]	206(25)
B^2_0	−172(21)	−298(17)	−215(19)	−301(17)
B^4_0	1462(31)	1416(26)	1494(31)	1447(29)
B^6_0	−2016(32)	−1941(25)	−2177(38)	−1929(31)
B^6_6	−1132(29)	−984(23)	−915(38)	−947(30)
b^2_0	0	0	55(25)	43(20)
b^4_0	0	0	−65(32)	−62(24)
b^6_0	0	0	135(34)	−29(28)
b^6_6	0	0	−181(34)	−42(27)
N[c]	127	139	127	139
σ/cm^{-1}	18.7	15.0	17.6	14.4

[a] All parameter values are given in cm^{-1}. [b] The crystal-field parameters, B^k_q and b^k_q, are defined with unit-tensor normalization properties. See eqn. (1) in text. [c] N is the number of energy levels included in the fitting calculations. [d] Parameter values shown in brackets were held fixed in the fitting calculation reported here.

TABLE II. Crystal-field Parameters for Nd^{3+} in NdF_3 and LaF_3 (C_{2v} Crystal-field Hamiltonian)[a]

Parameter[b]	Without SCCF		With SCCF	
	NdF_3	Nd^{3+}:LaF_3	NdF_3	Nd^{3+}:LaF_3
B^2_0	−156(15)	−247(18)	−166(15)	−248(17)
B^2_2	235(15)	194(21)	233(14)	184(19)
B^4_0	1345(22)	1378(25)	1391(21)	1441(26)
B^4_2	−141(25)	4(32)	−142(23)	15(29)
B^4_4	7(24)	119(33)	−20(22)	178(29)
B^6_0	−1900(24)	−1915(25)	−1851(31)	−2026(24)
B^6_2	−300(31)	−173(39)	−335(29)	−183(33)
B^6_4	457(26)	210(30)	444(24)	216(27)
B^6_6	−1112(20)	−1005(22)	−1109(27)	−850(28)
b^2_0	0	0	6(19)	43(20)
b^4_0	0	0	−98(22)	−117(25)
b^6_0	0	0	−11(27)	78(28)
b^6_6	0	0	−48(24)	−148(25)
N[c]	127	139	127	139
σ/cm^{-1}	11.2	13.0	10.9	11.5

[a] All parameter values are given in cm^{-1}. [b] The crystal-field parameters are defined with unit-tensor normalization properties. See eqn. (1) in text. [c] N is the number of energy levels included in the fitting calculations.

TABLE III. Energy Parameters for Nd^{3+}:$LiYF_4$[a]

Parameter[b]	Without SCCF	With SCCF
E_{ave}	24409(13)	24413(12)
F^2	72659(50)	72736(47)
F^4	52291(69)	52319(65)
F^6	35852(48)	35812(46)
α	21.1(2.2)	21.0(1.9)
β	−574(17)	−573(16)
γ	1482(26)	1486(24)
T^2	350(30)	322(29)
T^3	46(11)	49(9)
T^4	87(12)	87(11)
T^6	−299(16)	−292(15)
T^7	368(22)	351(20)
T^8	320(25)	302(24)
ζ_{so}	870(7)	869(7)
M^0	0.14(1.62)	0.28(1.73)
P^2	84(36)	120(33)
B^2_0	−559(27)	−550(27)
B^4_0	−1135(41)	−1056(44)
B^4_4	−1372(31)	−1514(32)
B^6_0	−35(40)	−317(47)
B^6_4	1383(32)	1308(40)
b^2_0	0	−10(33)
b^4_0	0	−66(41)
b^4_4	0	210(33)
b^6_0	0	286(43)
b^6_4	0	89(36)
N^c	129	129
σ/cm^{-1}	20.9	18.7

[a] All parameter values are given in cm^{-1}. [b] The crystal-field parameters, B^k_q and b^k_q, are defined with unit-tensor normalization properties. See eqn. (1) in text. [c] N is the number of energy levels included in the fitting calculations.

each case, inclusion of SCCF terms in the crystal-field Hamiltonian produces lower σ values. Ratios of b^k_q to B^k_q (denoted by c_{kq}) are listed in Table IV. Note that the SCCF results given in Table II do not include the b^2_2, b^4_2, b^4_4, b^6_2, and b^6_4 parameters. Values for these parameters were ill-determined when they were included in our data fits. Values of the free-ion parameters associated with the results given in Table II are not listed since they are nearly identical to those listed in Table I for the respective systems.

Comparisons between the results given in Tables I and II show that the C_{2v} model Hamiltonian for the crystal field in NdF_3 and Nd^{3+}:LaF_3 yields somewhat better data fits than the D_{3h} Hamiltonian. However, except for B^2_2, the 'extra' parameters in the C_{2v} model have relatively small values (when compared with the D_{3h} parameters of corresponding rank). Recall that these extra parameters (and their corresponding interaction operators) were included in the crystal-field Hamiltonian to simulate small distortions of the Nd^{3+} site symmetry away from D_{3h}. The lower-symmetry components of the crystal field appear to be more important in NdF_3 than in Nd^{3+}:LaF_3.

TABLE IV. Ratios of b^k_q to B^k_q (Defined as c_{kq})[a]

c_{kq}	NdF_3		Nd^{3+}:LaF_3		Nd^{3+}:$LiYF_4$
	D_{3h}	C_{2v}	D_{3h}	C_{2v}	D_{2d}
c_{20}	−0.25	(−0.04)	−0.14	−0.17	(0.02)
c_{40}	−0.04	−0.07	−0.04	−0.08	0.06
c_{44}					−0.14
c_{60}	−0.06	(0.01)	(0.02)	−0.04	−0.90
c_{64}					0.07
c_{66}	0.20	0.04	0.04	0.17	

[a] Values shown in parentheses are uncertain with respect to both magnitude and sign.

The most striking results obtained from our SCCF analyses of the NdF_3 and Nd^{3+}:LaF_3 data are the significantly different values determined for the c_{60} and c_{66} ratios (see Table IV). The b^k_q/B^k_q ratios are predicted to be q-independent within the framework of the superposition model for lanthanide–ligand interactions [12], assuming that the single-ligand contributions to both the one-electron and SCCF parts of $\mathcal{H}_{CF}$ have a similar distance dependence [13]. The c_{kq} ratios obtained for Nd^{3+}:$LiYF_4$ are even more striking in their q-dependence (see Table IV). In this case, the c_{60} ratio is more than an order-of-magnitude larger than c_{64} (and is of opposite sign), and the c_{44} ratio is larger than c_{40} (and also of opposite sign). We note from Table III that the SCCF has a dramatic effect on the fitted value for B^6_0.

Space constraints do not permit a fuller discussion of the results obtained in this study. The SCCF results reported here are of qualitative significance, but their implications regarding energy level fits within specific multiplet manifolds and their interpretation in terms of specific lanthanide–ligand interaction mechanisms will have to be addressed in a future communication.

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