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Re-examination of the $4f^3$ Energy Parameters for Several Systems with Neodymium–Oxygen Atom Coordination*

C. K. JAYASANKAR, F. S. RICHARDSON†, M. F. REID

Chemistry Department, University of Virginia, Charlottesville, Va. 22901, U.S.A.

P. PORCHER and P. CARO

Laboratoire des Elements de Transition dans les Solides, E.R. 210 du C.N.R.S., 1 Place A. Briand, 92195 Meudon-Bellevue Cédex, France

Crystal-field energy levels have been located and assigned for Nd^{3+} in a wide variety of crystalline materials in which the Nd^{3+} ions reside at sites surrounded by oxygen atoms (or anions). Much of the energy level data has been analysed in terms of parametrized Hamiltonians for the $4f^3$ electronic configuration of Nd^{3+} in the appropriate crystal-field symmetries, and parameter values obtained from calculated *versus* experimental energy level fits have been reported. In the present paper, we report results obtained from new parametric analyses carried out on energy level data reported previously in the literature for five different neodymium–oxygen coordinated systems. These analyses are based on a uniform (and common) set of parameters for the isotropic ('free-ion') part of the $4f^3$ electronic Hamiltonian, and the crystal-field Hamiltonian is defined to include spin-correlated crystal-field (SCCF) interactions [1–6].

The analyses performed in this study yield calculated *versus* experimental data fits superior to those reported previously for each of the systems examined. In most cases, however, the values obtained for the conventional, phenomenological crystal-field parameters are similar to those reported previously. Improvements in the data fits can generally be attributed to the introduction of additional terms (and parameters) in the free-ion Hamiltonian, and to small refinements in the crystal-field parameters. Inclusion of the phenomenological SCCF in our data fitting analyses invariably leads to better fits. However, it is not at all clear that the empirical data sets examined in this study are of sufficient quality (and quantity) to support a meaningful analysis of the SCCF. The SCCF results reported here should be considered with some caution and circumspection. They are suggestive, but not conclusive, regarding the importance of SCCF effects in the systems examined in this study.

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 ($k = 2, 4, 6$), $\alpha, \beta, \gamma, T^i$ ($i = 2, 3, 4, 6, 7, 8$), 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, 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 crystal-field Hamiltonian (including SCCF terms) was defined as follows:

$$\mathcal{H}_{CF} = \sum_{k,q} \sum_{i} [B_q^k u_q^k(i) + b_q^k S \cdot s_i u_q^k(i)] \qquad (1)$$

where i labels the 4f electrons; $u_q^k(i)$ is a one-electron unit-tensor operator; S and s_i are total spin and one-electron spin operators, respectively; and B_q^k and b_q^k are the one-electron and spin-correlated crystal-field parameters, respectively. Energy level data fits were carried out with and without the inclusion of the SCCF terms in eqn. (1). The ratio of b_q^k to B_q^k is denoted by c_{kq}.

All of the empirical energy level data analysed here were taken directly from the literature [7–13] and were used without making any reassignments. The systems examined were $NdAlO_3$ [7], A-Nd_2O_3 [8], $Nd(NO_3)_3 \cdot 6H_2O$ [9], $Nd_3Ga_5O_{12}$ [10] and $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ [11–13]. The structural properties and the coordination sites of neodymium have been described for each of these systems in the literature cited [7–13]. The crystal-field symmetries assumed for these systems in the present study are: D_3 for $NdAlO_3$; C_{3v} for A-Nd_2O_3; C_{3v} for $Nd(NO_3)_3 \cdot 6H_2O$; D_2 for $Nd_3Ga_5O_{12}$; and D_{3h} for $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$. These assumed (or 'effective') crystal-field symmetries deviate from the actual neodymium site symmetries only for $Nd(NO_3)_3 \cdot 6H_2O$ (C_s actual symmetry) and $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ (C_{3h} actual symmetry).

Hereafter in the text, we shall refer to $Nd(NO_3)_3 \cdot 6H_2O$ as neodymium nitrate (or Nd nitrate),

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†Author to whom correspondence should be addressed.

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to $Nd_3Ga_5O_{12}$ as neodymium gallium garnet (or NdGG), and to $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ as neodymium ethylsulfate (or NdES).

Results and Discussion

Parameter values obtained from our calculated *versus* experimental energy level fits are presented in Tables I–III along with the σ values for these fits. In each case, the σ values reported here for fits with or without the inclusion of SCCF terms in the Hamiltonian are significantly (but not dramatically) better than those reported previously for the respective systems [7–12]. Previous analyses did not include the spin–other-orbit and electrostatically correlated spin–orbit interactions in the free-ion Hamiltonian. Those interactions were included in the present study, although only one of the three parameters associated with each of these two types of interactions was treated as a free variable in performing data fits. The relevant freely varying parameters were M^0 and P^2. Inclusion of these interactions in the analyses improves the data fits and causes modest changes in the optimized crystal-field parameter values (relative to those reported previously). However, each of the M^0 and P^2 values shown in Tables I and III has a high degree of uncertainty, and these parameters must be considered ill-determined by the analyses carried out in this study.

The SCCF analyses were carried out with and without the isotropic energy parameters treated as free variables. In most cases, when these parameters were allowed to vary, their best-fit values were not significantly different from those obtained in the non-SCCF analyses. All of the SCCF results in Tables II and III were obtained using isotropic parameter values identical to those determined in the corresponding non-SCCF analyses. For each of the systems, NdES, $NdAlO_3$ and NdGG, inclusion of the SCCF had the greatest effects on the rank-six crystal-field parameters. This finding is in line with previous assertions that the rank-six SCCF interactions are likely to make more important contributions to the lanthanide crystal field than the rank-two and rank-four interactions [1–6]. However, it is important to stress that the phenomenological SCCF analyses reported here are not adequate for providing more than suggestive results regarding the possible importance of spin-correlated crystal-field effects. More refined data sets and methods of analysis are required to arrive at definitive conclusions (and to quantitate the SCCF effects accurately) [5].

No SCCF results are presented for the A-Nd_2O_3 and Nd nitrate systems. The free-ion parameters and one-electron crystal-field parameters (B^k_q) for these systems could not be refined sufficiently to support meaningful SCCF analyses. A similar problem was encountered in calculations performed on energy

TABLE I. Energy Parameters for Nd^{3+} in $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$, $NdAlO_3$, A-Nd_2O_3, and $Nd(NO_3)_3 \cdot 6H_2O$[a]

Parameter[b]	$Nd(C_2H_5SO_4)_3 \cdot 9H_2O$	$NdAlO_3$	A-Nd_2O_3	$Nd(NO_3)_3 \cdot 6H_2O$
E_{ave}	24324(15)	24257(9)	23648(49)	24393(57)
F^2	72335(56)	71822(32)	68865(170)	73137(196)
F^4	52884(66)	52447(51)	48107(273)	54501(317)
F^6	35822(72)	35197(53)	32008(287)	36930(337)
α	21.4(1.9)	20.7(1.1)	19.2(3.9)	20.8(2.8)
β	−644(11)	−629(8)	−624(27)	−603(22)
γ	1461(39)	1497(29)	2592(161)	930(188)
T^2	401(30)	203(14)	479(52)	205(39)
T^3	38(5)	36(5)	43(15)	22(11)
T^4	59(7)	84(6)	66(17)	82(15)
T^6	−299(14)	−276(7)	−278(24)	−302(20)
T^7	348(20)	277(11)	365(33)	318(28)
T^8	380(31)	261(13)	338(45)	203(36)
ζ_{so}	882(5)	878(4)	869(11)	877(9)
M^0	2.02(1.44)	0.92(1.27)	1.98(3.79)	0.92(3.02)
P^2	105(28)	58(18)	282(64)	121(50)
B^2_0	−209(18)	629(13)	1046(50)	−298(29)
B^4_0	−656(23)	627(19)	567(63)	−117(47)
B^4_3	0	−471(16)	1861(47)	657(39)
B^6_0	911(28)	2183(20)	−1088(68)	1944(52)
B^6_3	0	1238(19)	346(68)	−943(52)
B^6_6	−880(22)	1366(18)	−1001(65)	−239(72)
N[c]	61	116	90	98
σ (cm^{-1})	9.0	9.3	26.5	22.0

[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.

TABLE II. Comparisons of Crystal-Field Parameters Obtained With and Without the Inclusion of SCCF Interaction Terms[a]

Parameter[b]	$Nd(C_2H_5SO_4)_3 \cdot 9H_2O$		$NdAlO_3$	
	Without SCCF	With SCCF[d,e]	Without SCCF	With SCCF[d,e]
B^2_0	−209(18)	−201(14)	629(13)	637(12)
B^4_0	−656(23)	−579(22)	627(19)	647(19)
B^4_3	0	0	−471(16)	−461(17)
B^6_0	911(28)	755(26)	2183(20)	2321(23)
B^6_3	0	0	1238(19)	1174(21)
B^6_6	−880(22)	−983(22)	1366(18)	1332(23)
b^2_0	0	10(18)	0	−14(16)
b^4_0	0	−52(21)	0	−39(18)
b^4_3	0	0	0	−16(17)
b^6_0	0	157(22)	0	−146(20)
b^6_3	0	0	0	70(19)
b^6_6	0	102(20)	0	29(21)
N^c	61	61	116	116
σ (cm^{-1})	9.0	8.1	9.3	8.9
c_{20}		[−0.05]		[−0.02]
c_{40}		0.09		−0.06
c_{43}				[0.03]
c_{60}		0.21		−0.06
c_{63}				0.06
c_{66}		−0.10		0.02

[a,b,c]See corresponding footnotes in Table I. [d]The free-ion parameters were held fixed in the SCCF energy level fitting calculations. The assigned values were those listed in Table I for the respective systems. [e]$c_{kq} = b^k_q / B^k_q$. Values of c_{kq} given in brackets are uncertain with respect to both sign and magnitude.

TABLE III. Energy Parameters for $Nd_3Ga_5O_{12}$ (NdGG)[a]

Isotropic parameters[d]		Crystal-field parameters		
		Parameter[b]	Without SCCF	With SCCF
E_{ave}	24121(19)	B^2_0	465(25)	452(26)
F^2	70855(68)	B^2_2	−304(22)	−313(20)
F^4	52565(128)	B^4_0	−2741(35)	−2663(38)
F^6	37808(129)	B^4_2	458(36)	549(41)
α	21.5(2.7)	B^4_4	1189(33)	1155(37)
β	−681(17)	B^6_0	−1434(44)	−1390(52)
γ	1076(72)	B^6_2	285(37)	600(50)
T^2	710(39)	B^6_4	−1767(32)	−1699(33)
T^3	45(9)	B^6_6	−271(37)	11(47)
T^4	70(10)	b^2_0	0	−15(32)
T^6	−288(22)	b^2_2	0	50(27)
T^7	417(28)	b^4_0	0	−88(37)
T^8	592(39)	b^4_2	0	−47(40)
ζ_{so}	866(7)	b^4_4	0	19(34)
M^0	0.68(2.21)	b^6_0	0	−20(46)
P^2	77(33)	b^6_2	0	−296(45)
		b_4	0	−78(31)
		b^6_6	0	−248(40)
		N^c	104	104
		σ (cm^{-1})	16.0	14.8

[a,b,c]See corresponding footnotes in Table I. [d]These parameters were not treated as variables in the SCCF fitting calculations.

level data available for Nd^{3+} in the $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$ garnet hosts. Inclusion of the phenomenological SCCF in our data fits produced somewhat improved σ values and better agreement between calculated and observed crystal-field splittings within several multiplet manifolds. However, the magnitudes of at least a third of the c_{kq} ratios (b_q^k/B_q^k) were >0.5, which suggests that the fitted b_q^k parameters were absorbing effects unrelated to the SCCF.

The results reported here were obtained as part of a larger study aimed at characterizing lanthanide–oxygen interactions in a variety of coordination situations. Of particular interest in the present study was the determination of phenomenological one-electron crystal-field parameters from analyses that included simultaneous consideration of the two-electron interactions represented by the 'effective' SCCF operators in eqn. (1).

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References

1 B. R. Judd, *Phys. Rev. Lett., 39,* 242 (1977).
2 D. J. Newman, G. G. Siu and W. Y. P. Fung, *J. Phys. C, 15,* 3113 (1982).
3 G. G. Siu and D. J. Newman, *J. Phys. C, 16,* 7019 (1983).
4 H. Crosswhite and D. J. Newman, *J. Chem. Phys., 81,* 4959 (1984).
5 Y. Y. Yeung and D. J. Newman, *J. Phys. C, 19,* 3877 (1986).
6 M. F. Reid and F. S. Richardson, *J. Chem. Phys., 83,* 3831 (1985).
7 E. Antic-Fidancev, M. Lemaitre-Blaise, L. Beaury, G. Teste de Sagey and P. Caro, *J. Chem. Phys., 73,* 4613 (1980).
8 P. Caro, J. Derouet, L. Beaury and E. Soulie, *J. Chem. Phys., 70,* 2542 (1979).
9 P. Caro, D. Svoronos, E. Antic and M. Quarton, *J. Chem. Phys., 66,* 5284 (1977).
10 E. Antic-Fidancev, C. K. Jayasankar, M. Lemaitre-Blaise and P. Porcher, *J. Phys. C, 19,* 6451 (1986).
11 J. B. Gruber and R. A. Satten, *J. Chem. Phys., 39,* 1455 (1963).
12 Y. Kato, T. Nagai and A. Saika, *Bull. Chem. Soc. Jpn., 50,* 862 (1977).
13 C. A. Morrison and R. P. Leavitt, in K. A. Gschneider and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 5, North-Holland, New York, 1982, pp. 461–692 (see Section 5.26).