Crystal Field Levels of Neodymium and Erbium Ethylsulfate Nonahydrates

Yoshifumi KATO, Toshiyuki NAGAI, and Apollo SAIKA*

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657

**Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606*

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The energy levels of the Nd^{3+} ion in $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ and of the Er^{3+} ion in $Er(C_2H_5SO_4)_3 \cdot 9H_2O$ are calculated within the $4f^N$ configuration by the tensor operator method. The Hamiltonian containing a configuration interaction is diagonalized for the free ion levels and complete J-mixing is performed for the crystal field levels. The experimental "free-ion" energy levels of Nd^{3+} and Er^{3+} are fitted with a mean deviation of 70.8 cm^{-1} for 19 terms and 78.2 cm^{-1} for 22 terms, respectively. The crystal field parameters obtained for $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ and $Er(C_2H_5SO_4)_3 \cdot 9H_2O$ yield a mean deviation of 3.6 cm^{-1} for 43 levels and 3.6 cm^{-1} for 50 levels, respectively. The calculated Zeeman splitting factors (g values) in the direction along the crystal principal axis are in fair agreement with the experimental values.

It is well known that the crystal field theory provides a powerful tool for the energy level calculation of crystals containing rare earths, because the spin-orbit interaction of rare earths is not negligible as compared with the Coulomb or other interactions and f electrons in a crystal are generally well localized in an electrostatic field of the proper symmetry. On the reduction of the matrix elements of the Hamiltonian for rare earth crystals, the tensor operator method has been widely used instead of the early operator equivalent method, since the mathematical quantities necessary to apply the former method are now readily accessible in the form tabulated by Nielson and Koster.[1] Furthermore, the configuration interaction (CI) has a sizable effect on the energy levels of rare earths, and Rajnak[2] showed in the energy level calculation of trivalent neodymium and erbium ions that a least-squares fit by use of 4 or 5 parameters for CI reproduces the experimental "free-ion" levels with a deviation of about 50 cm^{-1}, which is less than half the deviation without CI.

Recently Crosswhite and Crosswhite[3] have carried out a crystal field calculation of Nd^{3+} doped in $LaCl_3$ by using as fully developed a Hamiltonian as appears feasible at the present time and by simultaneously diagonalizing the ion and crystal field parts of the Hamiltonian matrix. In their calculation, the experimental 101 crystal field levels have been fitted with a mean error of 8.1 cm^{-1} by using 24 adjustable parameters. Successively Carnall *et al.*[4] have made an energy level calculation of Pm^{3+} in the $LaCl_3$ host with similar accuracy to that by Crosswhite and Crosswhite.[3] In order to make such an extensive calculation, unambiguous experimental data must be available and the rare earths doped in $LaCl_3$ are probably the most adequate crystals among all the known salts. For these crystals, the absorption bands are sharp, there is very little evidence of superimposed crystal vibrations and furthermore strong fluorescences are observed in contrast with hydrated crystals.

For rare earth crystals which have been widely investigated, CI is expected to play a very important role in their electronic properties. However, previous energy level calculations for rare earth ethylsulfate crystals employ only partial J-mixing and no CI. In this paper crystal field level calculations of the neodymium and erbium ethylsulfate nonahydrates (Nd(ES) and Er(ES)) are carried out by simultaneously diagonalizing both the ion and crystal field parts of the Hamiltonian matrix with CI for the ion levels and complete J-mixing for the crystal field levels. Furthermore, the spectroscopic splitting factors (g factors) are evaluated from the wavefunctions obtained, and compared with the experimental values.

Calculational Procedure

Theoretical. The theoretical treatment for $4f^N$ configurations by use of the tensor operator method first introduced by Racah[5] and extended by Judd[6] is given in detail elsewhere.[7,8] Here the general procedure of calculations will be briefly outlined.

The $4f^N$ electronic states can be described satisfactorily in terms of intermediate coupling. Thus we may expand the wavefunction of a rare earth ion in crystals according to the Russell-Saunders coupling scheme to give

$$|\Psi\rangle = \sum_i a_i \phi_i | f^N, q, S, L, J, M\rangle, \qquad (1)$$

where q is an additional quantum number introduced to distinguish the electronic states. The Hamiltonian for an ion placed in a crystal field may be written as

$$H = H_{\text{coul}} + H_{\text{so}} + H_{\text{cry}} + H', \qquad (2)$$

where H_{coul}, H_{so}, and H_{cry} denote the Coulomb interaction between a pair of 4f electrons, the spin-orbit interaction and the potential due to the crystal field, respectively. The energy shift that gives the same contribution to all the levels belonging to a given configuration is neglected in the following treatment, because it does not affect the electronic structure of the configuration. The last term H' in Eq. 2 stands for an additional CI and may be taken as

$$\langle\Psi|H'|\Psi'\rangle = \delta(\Psi, \Psi')[\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)], \qquad (3)$$

where α, β, and γ are linear combinations of radial integrals discussed by other authors[9,10] and are treated as parameters. Further minor CI parameters are not included in Eq. 3.

The matrix elements of the Hamiltonian in Eq. 2 can be reduced by the tensor operator method. Then the matrix element of the electrostatic interactions within the $4f^N$ configuration can be written as a linear combination of the Slater radial integrals F_n,

$$\langle f^N qSLJM|\sum_{i>j} e^2/r_{ij}|f^N q'SLJM\rangle = \sum_n p_n F_n(4f, 4f),$$
$$(n=2,\ 4,\ \text{and}\ 6), \tag{4}$$

where the coefficient p_n represents the angular part of the interaction. Similarly the matrix element of the spin-orbit interactions can be reduced to

$$\langle f^N qSLJM|\zeta_{4f}\sum_i(\boldsymbol{s}_i\cdot\boldsymbol{l}_i)|f^N q'S'L'J'M'\rangle$$
$$= \delta(J, J')\delta(M, M')2\sqrt{21}\zeta_{4f}(-1)^{J+L+S'}$$
$$\times\begin{Bmatrix} L & L' & 1 \\ S' & S & J \end{Bmatrix}\langle f^N qSL\|\boldsymbol{V}^{(11)}\|f^N q'S'L'\rangle, \tag{5}$$

where ζ_{4f} is the spin-orbit radial integral with respect to a 4f electron and $\boldsymbol{V}^{(11)}$ is the double tensor defined by Racah.5) The matrix elements of electrostatic interactions and those of spin-orbit interactions of the $4f^3$ configuration are already tabulated by Nielson and Koster,1) and Judd and Loudon,11) respectively. We need only to evaluate the matrix elements of the crystal field potential. This may also be expanded by the irreducible tensor operator $\boldsymbol{C}_q^{(k)}$ as

$$H_{cry} = \sum_i \sum_{k,q} B_q^k(\boldsymbol{C}_q^{(k)})_i, \tag{6}$$

in which the summation over i is for all the electrons and the coefficient B_q^k is the crystal field parameter. Then the matrix element of H_{cry} will be reduced to

$$\langle f^N qSLJM|H_{cry}|f^N q'S'L'J'M'\rangle$$
$$= \delta(S, S')\sum_{k,q} 7B_q^k(-1)^{2J+S+L'+k-M-1}$$
$$\times[(2J+1)(2J'+1)]^{1/2}\begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix}\begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix}$$
$$\times\langle f^N qSL\|\boldsymbol{U}^{(k)}\|f^N q'SL'\rangle, \tag{7}$$

in which the doubly reduced matrix elements of the unit tensor operator $\boldsymbol{U}^{(k)}$ are given in the table of Nielson and Koster.1)

Once the eigenvectors are determined by diagonalizing the Hamiltonian, we can obtain the z component of the g value as

$$g_z = \langle\Psi|\mu_z|\Psi\rangle = \sum_i a_i^2 M g_i(qSLJ), \tag{8}$$

where μ_z is the component of the magnetic dipole operator along the principal axis of a crystal and $g_i(qSLJ)$ denotes the Lande g factor for an ion level.

Application. The Nd^{3+} and Er^{3+} ions in ethylsulfates have $4f^3$ and $4f^{11}$ configurations, respectively. Since these two configurations are complementary to one another, the Er^{3+} ion has the same number and kind of states as the Nd^{3+} ion, for which there are 41 different $|JM\rangle$ states. According to the crystal structure of rare earth ethylsulfates determined by X-ray diffraction,12) the space group is $P6_3/m$ (C_{6h}^2) and the local symmetry about a rare earth ion is D_{3h} as far as only the nearest-neighbor oxygen atoms of 9 crystalline waters are concerned.13) The crystal field of the D_{3h} symmetry is expanded as

$$H_{cry} = B_0^2\boldsymbol{C}_0^{(2)} + B_0^4\boldsymbol{C}_0^{(4)} + B_0^6\boldsymbol{C}_0^{(6)}$$
$$+ B_6^6(\boldsymbol{C}_6^{(6)} + \boldsymbol{C}_{-6}^{(6)}). \tag{9}$$

Following Hellwege,14) each ion level under this symmetry may be classified in three irreducible representations specified by the crystal quantum number η. As a result, the secular determinant for crystal levels can be reduced to two 60×60 matrices for $\eta = \pm 1/2$ and $\pm 5/2$ and one 62×62 matrix for $\eta = \pm 3/2$ by the usual group-theoretical procedure. Each crystal level has, of course, a twofold degenerate Kramers' pair.

After the subprograms for the 3-j and 6-j symbols were checked to agree with the tables already published,15) the eigenvalue problem was solved by machine. With the parameters determined by Eisenstein16) for the energy calculation of Nd^{3+} in $LaCl_3$ as a test run, our results reproduced those of Eisenstein with an accuracy of five significant figures. The actual determination of the parameters was made in the following manner. First, the Hamiltonian without H_{cry} in Eq. 2 was diagonalized to determine the intermediate coupling parameters (F_2, F_4, F_6, and ζ_{4f}) and the CI parameters (α, β, and γ) by fitting the calculated values to the centers of gravity of the experimental levels by an iterative procedure. Secondly, the diagonalization of the entire Hamiltonian with all the J-mixing was performed iteratively by adjusting the crystal field parameters (B_0^2, B_0^4, B_0^6, and B_6^6). Finally, a minor adjustment of all the parameters was made by a least-squares method. All the calculations were performed by the use of a FACOM 230-75 computer at Kyoto University.

Results and Discussion

The parameters used in the final calculation and the standard deviations are given in Tables 1 and 2 for Nd(ES) and Er(ES), respectively together with those obtained by others. Here, the root mean square (rms) deviation is defined as

$$\sigma = [\sum_i \Delta_i^2/N]^{1/2}, \tag{10}$$

in which Δ_i is the difference between the observed and

TABLE 1. PARAMETERS USED IN THE FINAL CALCULATION AND ROOT MEAN SQUARE DEVIATION IN $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$a)

Parameter	Present	Gruber & Satten
F_2	329.3	331.33
F_4	49.90	47.956
F_6	5.338	5.313
ζ_{4f}	873.5	880.11
α	1.40±0.20	—
β	−200.0±30.0	—
γ	0.0	—
B_0^2	142.8	116.8
B_0^4	−587.4	−545.6
B_0^6	−757.1	−683.2
B_6^6	601.5	626.4
rms deviation		
For center of gravity	70.8(19)	104.7(19)b)
For crystal level	2.9(28) 3.6(43)	7.7(37)b)

a) Units in cm^{-1}. The number of energy levels fitted are given in parentheses. b) See Ref. 21.

Table 2. Parameters used in the final calculation and root mean square deviation in $Er(C_2H_5SO_4)_3 \cdot 9H_2O$[a)]

Parameter	Present	Erath	Rajnak	Wheeler & Hill
F_2	445.5	433.64	446.16	
F_4	69.30	67.522	69.131	
F_6	7.715	7.090	7.7010	
ζ_{4f}	2355.0	2471.0	2353.4	
α	17.50	—	17.49	
β	−690.3	—	−690.3	
γ	0.0	—	$Y(22:1)=-4560.$	
B_0^2	228.7	251.60		237.6
B_0^4	−631.2	−649.52		−591.2
B_0^6	−515.3	−496.92		−486.4
B_6^6	412.0	407.60		395.7
rms deviation				
For center of gravity	78.2(22)	285.1(10)	50.0(22)	
For crystal level	3.6(50)	3.4(46)		

a) See the footnote (a) in Table 1.

calculated values of the ith level and N is the number of levels. The calculated numerical results are presented in Tables 3 and 4 for Nd(ES) and Er(ES), respectively.

Nd(ES). Among the experimental energy levels of Nd(ES) reported by several authors,[17–19)] we use the 19 electronic terms proposed by Gruber and Satten.[19)] For the definitely assigned 9 electronic terms, the centers of gravity by Gruber and Satten differ within 6 cm^{-1} from those proposed by others. The discrepancy is smaller than the final rms deviation and should not have any significant effect on the final results. Since the calculated terms are not so sensitive to the variation of CI parameters, both α and β contain a considerable amount of error; especially γ is not determined because the electronic term (100)(10) ^{2}F affected strongly by γ has not been observed in Nd(ES). As can be seen in Table 1, while there exist only small differences between the intermediate coupling parameters by ours and those by Gruber and Satten, the rms deviation is considerably improved by the inclusion of the CI parameters α and β. A further improvement should be expected by introducing other higher-order interactions for CI and the increasing the number of levels available. For several crystal levels, both the assignments and splittings by Gruber and Satten[19)] differ slightly from those by Dieke.[20)] In the present calculation the 28 reliable crystal field levels for 9 electronic terms by Dieke[20)] could be fitted with an rms deviation of 2.9 cm^{-1}, and the 43 levels containing ambiguous ones fitted with 3.6 cm^{-1}. The calculation by Gruber and Satten yielded an rms deviation of 7.7 cm^{-1} for 37 levels by first-order perturbation treatment with only partial J-mixing for the ground multiplet.[21)] The crystal field parameters thus obtained are somewhat different from those of Gruber and Satten; especially for the B_0^2 parameter the difference exceeds 20 percent. This is due to their use of only the ground state multiplet levels for fitting.

From the eigenfunctions obtained, it became clear that through spin-orbit interactions $^2P_{3/2}$, $^2G_{7/2}$, and $^2G_{9/2}$ couple strongly with $^2D_{3/2}$, $^4G_{7/2}$, and $^4G_{9/2}$, respectively, whereas the strong coupling through J-mixing, in particular, occurs between the terms with $\Delta J=1$ and 6. Comparison of the calculated g values with the

Table 3. Experimental and calculated values of the energy levels and g values for $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$[a)]

Term	Center of gravity			Crystal level relative to center				$\lvert g \rvert$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
$^4I_{9/2}$	0	0	0	5	−178.7	−179.5	0.8	1.75	1.96
				3	−29.2	−25.1	−4.1		1.44
				1	−24.7	−24.4	−0.3		0.35
				5	100.3	97.3	3.0		1.21
				3	132.3	131.7	0.6		0.79
$^4I_{11/2}$		1860.8		3		−61.6			3.75
				1		−13.1			1.74
				5		−11.5			2.26
				3		26.5			0.86
				5		26.5			1.30
				1		33.2			3.10
$^4I_{13/2}$		3834.8		1		−88.0			4.97
				3		−51.5			3.29
				5		−12.5			0.82
				1		−6.6			0.89
				3		36.9			0.03
				1		44.2			5.75
				5		77.5			0.28
$^4I_{15/2}$		5894.5		1		−222.7			3.41
				1		−139.2			0.15
				3		−99.5			0.91

Table 3. (Continued)

Term	Center of gravity			Crystal level relative to center				$\lvert g \rvert$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b]	Calcd
				5		−45.0			0.18
				1		29.2			1.46
				3		107.7			6.76
				3		150.8			0.44
				5		218.7			1.01
$^4F_{3/2}$	11368.0	11443.9	−75.9	1	−9.6	−9.0	−0.6	0.26	0.22
				3	9.6	9.0	0.6		0.64
$^4F_{5/2}$	12404.0	12472.8	−68.8	1	−23.2	−18.1	−5.1		0.52
				5	3.0	−0.5	2.5		2.55
				3	20.2	18.6	1.6		1.50
$^4H_{9/2}$	12525.0	12617.9	−92.9	5		−82.6			1.58
				3		−72.7			0.36
				3	(26.2)	27.9	(−1.7)		2.60
				1	(33.8)	31.3	(2.5)		0.50
				5		96.1			2.57
$^4F_{7/2}$	13367.0	13457.2	−90.2	5	−51.9	−50.4	−1.5		0.55
				1	−41.7	−43.8	2.1		0.61
				3	38.4	42.1	−3.7		1.81
				5	55.2	52.3	2.9		1.75
$^2S_{3/2}$	13454.0	13387.1	66.9	1	−1.7	−1.4	−0.3		0.98
				3	1.7	1.4	0.3	2.53[c]	2.94
$^4F_{9/2}$	14640.0	14719.1	−79.1	5	(−31.2)	−29.4	(1.8)		2.52
				5	−25.5	−24.9	−0.6		1.30
				3	−0.3	−0.2	−0.1		1.83
				1	16.5	13.4	3.1		0.62
				3	40.5	41.1	−0.6		5.52
$^4H_{11/2}$	15842.0	15867.4	−25.4	3		−25.1			3.42
				1		−18.1			0.48
				5		−15.1			1.30
				3		10.5			0.15
				1	(13.0)	14.5	(−1.5)		5.95
				5	(34.3)	33.3	(1.0)		0.22
$^4G_{5/2}$	17118.0	17046.7	71.3	1	(−58.6)	−47.8	(−10.8)	0.72[c]	0.30
				5		−20.1			1.01
				3	(77.1)	67.9	(9.2)		0.88
$^2G_{7/2}$	17239.0	17222.0	17.0	3		−35.6			1.36
				5	(−17.8)	−22.4	(4.6)		0.45
				1	(19.4)	21.5	(−2.1)		0.44
				5	(37.6)	36.5	(1.1)		0.10
$^2K_{13/2}$		18892.5		5		−75.9			3.13
				3		−55.9			3.44
				1		−41.7			4.99
				5		−35.5			2.07
				1		2.0			6.02
				3		101.9			1.38
				1		105.1			0.48
$^4G_{7/2}$	18996.0	18965.9	30.1	3	(−82.2)	−88.6	(6.4)		0.65
				1	(−22.4)	−26.5	(4.1)		0.38
				5	(13.9)	19.7	(5.8)		2.15
				5		95.4			1.29
$^4G_{9/2}$	19408.0	19391.9	16.1	3	(−17.6)	−16.6	(1.0)		3.92
				1		−4.6			0.56
				5		−2.3			3.71
				3	(11.9)	10.3	(1.6)		0.51
				5		13.2			2.62

TABLE 3. (Continued)

Term	Center of gravity			Crystal level relative to center				$\|g\|$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
$^2K_{15/2}$		20842.7		1		−43.3			6.72
				3		−37.0			4.53
				1		−28.6			5.63
				5		−14.7			3.47
				3		−0.9			6.85
				5		25.9			2.39
				3		46.9			1.62
				1		51.7			0.47
$^2G_{9/2}$	20982.0	21019.1	−37.1	1	(−59.8)	−57.7	(−2.1)		0.43
				3	(−20.8)	−20.1	(−0.7)		1.64
				3		11.3			4.74
				5		19.8			0.04
				5		46.7			1.13
$^2D_{3/2}$	21116.0	21232.7	−116.7	1	−8.1	−12.6	4.5		0.55
				3	8.1	12.6	−4.5		2.00
$^4G_{11/2}$	21438.0	21404.1	33.9	1		−109.3			0.92
				3		−57.3			1.20
				1		−38.8			5.20
				3		39.9			2.41
				5		46.4			1.05
				5		119.1			2.27
$^2P_{1/2}$	23180.0	23045.7	134.3	1				0.37	0.31
$^2D_{5/2}$	23730.0	23745.0	−15.0	1	−19.5	−26.8	6.3	0.59	0.60
				3	−1.2	5.8	7.0		1.80
				5		21.0			2.99
$^2P_{3/2}$	26102.0	26113.4	−11:4	1	−12.4	−14.8	2.4	0.54	0.55
				3	12.4	14.8	−2.4		1.61
$^4D_{3/2}$	28049.0	28174.2	125.2	1	−3.4	−2.3	−1.1		0.56
				3	3.4	2.3	1.1		1.73
$^4D_{5/2}$		28391.7		3		−58.8			1.99
				5		−7.3			3.33
				1		66.1			1.07
$^2I_{11/2}$		28555.6		1		−135.6			3.32
				1		−19.7			0.35
				3		−4.5			1.13
				3		40.2			3.97
				5		44.6			2.22
				5		75.0			3.18
$^4D_{1/2}$		28754.0		1					0.01
$^2L_{15/2}$		29179.3		3		−102.6			6.97
				5		−83.7			1.73
				3		−75.7			3.63
				1		−17.6			3.62
				1		−5.1			4.72
				5		47.6			0.80
				3		96.1			0.91
				1		141.0			0.32
$^2I_{13/2}$		29883.1		1		−118.3			6.68
				5		−11.4			0.80
				1		−5.9			0.65
				3		−5.1			0.75
				5		40.6			1.87
				1		42.0			4.43
				3		58.1			3.96
$^4D_{7/2}$		30426.9		5		−65.3			4.98

TABLE 3. (Continued)

Term	Center of gravity			Crystal level relative to center				$\lvert g \rvert$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
				1		12.9			0.71
				3		26.2			2.15
				5		26.2			3.65
$^2L_{17/2}$		30658.9		5		−123.9			8.83
				3		−48.1			3.81
				5		−38.1			1.93
				1		−28.8			5.24
				3		−23.0			7.32
				1		7.3			6.23
				5		57.5			0.93
				3		86.6			1.22
				1		110.5			0.59
$^2H_{9/2}$		32523.4		3		−63.8			2.68
				5		−50.8			1.31
				3		8.1			0.04
				1		36.8			0.46
				5		69.7			2.22
$^2D_{3/2}$		33329.4		3		−5.3			1.28
				1		5.3			0.39
$^2H_{11/2}$		33838.4		5		−132.9			0.19
				1		−65.1			5.30
				3		−31.0			0.46
				5		36.4			1.25
				1		78.4			0.06
				3		114.2			3.56
$^2D_{5/2}$		34546.9		3		−19.8			1.69
				5		−13.7			2.96
				1		33.5			0.53
$^2F_{5/2}$		39466.3		5		−20.2			2.25
				3		−9.8			1.36
				1		30.0			0.45
$^2F_{7/2}$		40870.4		5		−47.9			1.38
				5		10.5			2.51
				1		12.4			0.57
				3		25.0			1.71
$^2G_{9/2}$		47622.7		5		−53.9			2.91
				3		−37.9			4.29
				1		−7.6			0.56
				3		42.5			0.97
				5		56.9			1.81
$^2G_{7/2}$		48509.1		5		−74.5			1.44
				1		−11.5			0.45
				5		22.5			0.55
				3		63.5			1.33
$^2F_{7/2}$		68447.2		5		−108.8			3.77
				3		16.6			1.71
				1		25.8			0.57
				3		66.4			2.63
$^2F_{5/2}$		69531.2		5		−78.7			2.14
				1		12.0			0.43
				3		66.7			1.29

a) Energy units in cm^{-1}. Diff=Exptl−Calcd. When the location of the center of a term is not known experimentally, the position which yields the best agreement with the calculation is taken as the center assumed in column 2. Values in parentheses are less reliable. b) The values from the Zeeman effect (Ref. 17). Here, $s_1=2|g|$. c) The values are increased by 9% according to the footnote in Table 3 of Ref. 17.

TABLE 4. EXPERIMENTAL AND CALCULATED VALUES OF THE ENERGY LEVELS AND g VALUES FOR $Er(C_2H_5SO_4)_3 \cdot 9H_2O$[a)]

Term	Center of gravity			Crystal level relative to center				$\|g\|$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
$^4I_{15/2}$	0	0	0	5	−147.1	−148.9	1.8	0.76	0.71
				3	−103.1	−105.3	2.2	1.00	2.07
				3	−72.4	−74.5	2.1	6.60	5.20
				1	−36.9	−32.7	−4.2		0.49
				5	25.5	25.9	−0.4		0.49
				3	68.7	62.8	5.9		1.89
				1	108.9	112.8	−3.9		2.94
				1	156.9	159.9	−3.0		5.22
$^4I_{13/2}$		6424.4		5		−52.0			0.48
				3		−37.2			0.89
				1		−35.9			3.83
				1		−14.3			3.59
				5		12.3			1.58
				3		50.0			4.20
				1		77.1			5.76
$^4I_{11/2}$	10113.0	10040.6	72.4	1	−13.9	−20.2	6.3		0.23
				3	−13.0	−19.5	6.5		1.24
				5	−12.0	−13.8	1.8		1.88
				1	−10.3	2.9	−13.2		4.71
				5	12.4	13.4	−1.0		2.87
				3	37.1	37.6	−0.5		4.20
$^4I_{9/2}$	12366.7	12279.5	87.2	3	−87.6	−91.0	3.4		1.10
				5	−73.9	−76.4	2.5		1.35
				3	11.2	10.2	1.0		1.58
				1	26.4	23.9	2.5		0.44
				5	123.9	132.9	−9.0		2.26
$^4F_{9/2}$	15207.4	15196.5	10.9	3	−48.5	−48.0	−0.5	2.42	2.95
				1	−15.1	−17.3	2.2	0.58	0.57
				5	−6.0	−8.7	2.7		2.87
				3	22.7	22.4	0.3	0.78	0.52
				5	44.7	51.6	−5.6		1.74
$^4S_{3/2}$	18327.0	18571.1	−244.1	3	−13.0	−13.2	0.2	2.47	2.53
				1	13.0	13.2	−0.2		0.85
$^2H_{11/2}$	19087.3	19157.4	−70.1	5	−65.1	−59.7	−5.4		0.53
				5	−17.3	−10.8	−6.5		0.59
				3	−7.7	−9.7	2.0		1.43
				1	11.3	11.0	0.3		5.36
				3	24.0	24.5	−0.5		1.95
				1	54.9	44.1	10.8		0.30
$^4F_{7/2}$	20457.6	20400.6	57.0	5	−48.3	−49.0	0.7		2.13
				3	−16.6	−20.6	4.0	1.85	1.80
				5	18.4	23.3	−4.9		0.92
				1	46.4	46.3	0.1		0.60
$^4F_{5/2}$	22121.8	22056.7	121.5	3	−13.1	−10.0	−3.1	1.56	1.57
				5	1.8	−3.5	5.3		2.62
				1	11.2	13.5	2.3		0.52
$^4F_{3/2}$	22461.1	22425.1	36.0	3	−23.4	−17.5	−5.9	1.05	1.13
				1	23.4	17.5	5.9		0.37
$^2G_{9/2}$	24515.6	24412.2	103.4	3	−80.8	−76.1	−4.7	1.83	2.27
				5	−58.6	−61.6	3.0	1.60	1.56
				3	1.6	4.6	−3.0	1.50	0.96
				1	24.4	28.6	−4.2	0.15	0.54
				5	116.6	104.5	12.1		2.64
$^4G_{11/2}$	26348.5	26361.7	−13.2	5	−59.1	−61.6	2.5		2.35
				3	−23.2	−22.1	−1.1		3.93

Table 4. (Continued)

Term	Center of gravity			Crystal level relative to center				$\lvert g \rvert$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
				5	−13.9	−19.5	5.6		1.15
				3	16.9	20.6	3.7		0.34
				1	22.3	26.3	−4.0		4.82
				1	57.5	56.5	1.0		1.17
$^4G_{9/2}$		27313.8		5		−23.0			2.73
				3		2.3			0.86
				1		3.0			0.55
				5		3.3			1.64
				3		14.4			4.18
$^2K_{15/2}$		27697.6		1		−133.5			0.52
				3		−103.4			1.55
				5		−45.5			2.38
				3		1.9			7.94
				5		34.3			3.43
				1		62.3			6.80
				3		85.4			4.71
				1		98.1			5.71
$^2G_{7/2}$		27942.6		5		−14.7			2.44
				1		−4.3			0.47
				5		6.2			1.48
				3		12.8			1.41
$^2P_{3/2}$		31642.8		3		−22.2			1.57
				1		22.2			0.54
$^2K_{13/2}$		32944.8		1		−95.1			0.50
				3		−72.1			1.40
				5		−40.4			2.16
				1		2.4			6.06
				5		25.1			3.12
				3		84.3			4.23
				1		95.8			5.16
$^4G_{5/2}$		33247.0		3		−53.1			0.88
				5		15.4			1.49
				1		37.7			0.29
$^2P_{1/2}$		33506.2		1					0.32
$^4G_{7/2}$		33865.5		5		−48.1			1.17
				5		1.1			2.11
				1		21.7			0.47
				3		25.3			1.42
$^2D_{5/2}$		34778.0		5		−20.1			2.99
				1		−1.8			0.60
				3		21.9			1.80
$^2H_{9/2}$		36369.6		5		−110.7			2.68
				3		−26.7			3.04
				1		−14.5			0.51
				3		74.4			0.05
				5		77.5			1.66
$^4D_{5/2}$		38517.2		1		−13.2			0.63
				5		−9.4			3.16
				3		22.6			1.89
$^4D_{7/2}$		39104.6		1		−38.8			0.71
				3		−34.6			2.12
				5		−20.0			3.49
				5		93.4			4.90
$^2I_{11/2}$		41036.9		3		−76.2			2.84
				1		−60.3			0.24

TABLE 4. (Continued)

Term	Center of gravity			Crystal level relative to center				$\|g\|$	
	Exptl	Calcd	Diff	2γ	Exptl	Calcd	Diff	Exptl[b)]	Calcd
				5		−27.2			1.04
				3		17.9			0.09
				1		63.6			5.15
				5		82.2			0.06
$^2L_{17/2}$		41567.7		1		−129.5			0.48
				3		−108.2			1.32
				5		−78.9			1.30
				5		−4.9			2.35
				3		20.2			4.45
				1		34.9			4.77
				1		38.2			5.88
				3		69.4			7.89
				5		158.8			8.99
$^4D_{3/2}$		42136.8		3		−10.4			1.58
				1		10.4			0.53
$^2D_{3/2}$		42893.5		1		−13.7			0.55
				3		13.7			1.64
$^2I_{13/2}$		43680.9		3		−74.0			3.42
				1		−60.9			4.11
				5		−57.4			1.25
				1		−0.5			1.16
				3		11·7			0.23
				5		22.3			0.18
				1		158.8			6.86
$^4D_{1/2}$		46853.8		1					0.03
$^2L_{15/2}$		47696.1		3		−87.4			0.73
				1		−81.3			0.29
				5		−54.4			2.56
				3		−42.9			1.37
				5		−30.7			1.92
				1		−18.3			0.13
				1		86.2			0.38
				3		228.6			4.11
$^2H_{9/2}$		47857.4		3		−61.3			2.83
				5		−47.5			2.92
				5		−39.1			1.71
				1		55.6			1.34
				3		92.3			3.32
$^2D_{5/2}$		48971.2		1		−69.6			0.61
				5		31.0			3.03
				3		38.6			1.81
$^2H_{11/2}$		50948.6		5		−65.1			3.33
				5		−44.9			2.29
				3		−22.7			4.56
				3		−5.9			1.45
				1		22.4			0.52
				1		116.2			5.70
$^2D_{3/2}$		55009.5		1		−24.5			0.44
				3		24.5			1.34
$^2F_{7/2}$		55788.5		3		−21.8			1.72
				5		−3.2			1.48
				1		−1.6			0.57
				5		26.7			2.79
$^2F_{5/2}$		63402.3		1		−15.0			0.45
				3		1.4			1.35

TABLE 4. (Continued)

Term	Center of gravity			Crystal level relative to center				$\lvert g \rvert$	
	Exptl	Calcd	Diff	2η	Exptl	Calcd	Diff	Exptl[b)]	Calcd
				5		13.6			2.25
$^2G_{7/2}$		65426.8		1		−38.4			0.45
				3		−21.6			1.34
				5		22.4			0.51
				5		37.6			1.40
$^2G_{9/2}$		69535.0		3		−39.1			1.62
				1		−30.7			0.55
				5		−27.7			2.42
				5		32.4			3.53
				3		65.1			4.93
$^2F_{5/2}$		95149.8		3		−78.4			1.29
				1		−32.0			0.43
				5		110.4			2.14
$^2F_{7/2}$		98542.6		3		−77.4			1.71
				5		−64.0			2.85
				1		−32.7			0.57
				5		174.1			3.99

a) Energy units in cm^{-1}. Diff=Exptl−Calcd. b) The values from the Zeeman effect (Ref. 24).

experimental ones is possible only for a few levels as can be seen in the last two columns of Table 3. The agreement is fairly good except the $^4G_{5/2}$ ($\eta=\pm 1/2$) level, in which the experimental value is over twice as large as the calculated one. The resolution of this point must await further studies. Eisenstein[16)] compared the g values of Nd^{3+} in $LaCl_3$ calculated by complete J-mixing with the experimental ones, and found the calculated values in good agreement with the experimental ones for all but 3 of 33 levels. Thus the g values in the present calculation should be fairly reliable and can be taken as a reference when the experimental values are not available.[22,23)]

Er(ES). The spectrum of Er(ES) has been reported by several authors.[24–27)] Wheeler and Hill[27)] observed directly in the far infra-red the crystal field splitting of the $^4I_{15/2}$ ground multiplet and determined the crystal field parameters. Erath[25)] calculated the crystal field parameters by a first-order perturbation on the ground multiplet in Er(ES) using the electrostatic and spin-orbit interaction parameters obtained by Wong.[28)] He computed the splitting of excited levels due to the crystal field using these crystal parameters. Rajnak[2)] made a CI calculation for the ion levels of Er^{3+} in Er(ES) by use of both the linear parameters, α, β, and γ, and the nonlinear parameter $Y(kk'\colon l')$. The latter parameter results from the interactions of a configuration with the configurations differing from f^N in the quantum numbers of only one electron.[9)]

As seen in Table 2, the inclusion of CI parameters reduces the rms deviation for the ion levels to less than one third of that without CI. Furthermore an improvement of about 30 cm^{-1} is achieved by including only one nonlinear parameter $Y(22\colon 1)$. This fact shows that CI effects are highly important for the ion levels. There are several differences between the present assignment of some electronic terms and those by previous authors, especially for the levels with $J=9/2$, of which the eigenvectors are given in Table 5. The present assignment of terms for higher levels over 30000 cm^{-1} is markedly different from that by Erath[25)] in some cases; for example, the present $^2P_{3/2}$, $^4G_{5/2}$, and $^2P_{1/2}$ terms are assigned to the $^3D_{3/2}$, $^2P_{1/2}$, and $^4G_{5/2}$ terms by Erath, respectively. For the crystal field splitting, the present result including complete J-mixing does not show any improvement over Erath's result in contrast with Nd(ES). On the other hand, the centers of gravity of multiplets with complete J-mixing shift within 10 cm^{-1} from the ion levels without J-mixing among all the terms except the higher two terms, $^2L_{15/2}$ and $^2H_{9/2}$,

TABLE 5. EIGENVECTORS OF THE TERMS WITH $J=9/2$ IN $Er(C_2H_5SO_4)_3 \cdot 9H_2O$

Energy (cm^{-1})	Eigenvector							Assignment[b)]			
	$\lvert ^4F\rangle$	$\lvert ^2G(1)\rangle$	$\lvert ^2G(2)\rangle$	$\lvert ^4G\rangle$	$\lvert ^2H(1)\rangle$	$\lvert ^2H(2)\rangle$	$\lvert ^4I\rangle$	(A)	(B)	(C)	(D)
12366.7	0.3509	0.2737	−0.2206	0.0109	0.1940	−0.4162	−0.7364	^4I	^4I	^4I	^4F
15207.4	0.7736	0.2932	−0.2224	0.0905	0.0014	0.0780	0.5019	^4F	^4F	^4F	^4I
24515.6	−0.4915	0.4349	−0.3929	0.2484	0.2642	−0.4040	0.3467	^2G	^2H	^2H	^2G
27313.2[a)]	−0.0200	0.0108	−0.0526	0.8906	−0.0998	0.3818	−0.2186	^4G	^2G	^4G	^4G
36366.8[a)]	−0.1891	0.4872	−0.3970	−0.3561	−0.2918	0.5661	−0.1921	^2H	—	^2H	—

a) The calculated values. b) (A), the present results; (B), Dieke (Ref. 20); (C), Rajnak (Ref. 2); (D) Erath (Ref. 25).

with a shift of about 50 cm^{-1}. This means that J-mixing for Er(ES) is not so significant as for Nd(ES). Since the magnitude of the spin-orbit coupling of Er^{3+} ($\approx$2350 cm^{-1}) is considerably larger than that of Nd^{3+} ($\approx$870 cm^{-1}) and then the ion levels of Er^{3+} are more separated than those of Nd^{3+}, the mixing among the ion levels with different J due to a crystal field becomes smaller for Er(ES) than for Nd(ES). Thus it will generally be the case that the effect of J-mixing for crystal levels is not so important for electron holes with large spin-orbit interaction. In Table 4, good agreement between the calculated g values and those by the Zeeman experiment is found except for a few cases as in the case of Nd(ES).

In conclusion, it will be stated that: (1) CI for the ion levels of both Nd(ES) and Er(ES) makes a remarkable improvement. (2) Inclusion of complete J-mixing for the crystal field levels yields some improvement for Nd(ES) but not so for Er(ES). This originates exclusively from the fact that the ion levels of Er(ES) with large spin-orbit coupling are substantially well separated, and mixing among different J levels is small due to weak perturbation by a crystal field. (3) The g values obtained by the present procedure may be fairly reliable and of practical usage in some cases.

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