Energy Levels and g Values of Some Rare Earth Crystals with f^2 Configuration

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The energy levels of the rare earth ions in praseodymium ethyl sulfate, magnesium praseodymium nitrate, and thulium ethyl sulfate crystals are calculated by using an extended Hamiltonian for $4f^2$ configuration. The Hamiltonian includes two-body electrostatic interactions, spin-other-orbit interactions and two-body pseudo-magnetic interactions as configuration-mixing parameters in addition to the Slater, spin-orbit coupling and crystal-field parameters. The standard deviations for praseodymium ethyl sulfate, magnesium praseodymium nitrate and thulium ethyl sulfate are respectively 10.1 cm^{-1} for 25 observed levels by using 13 parameters, 3.8 cm^{-1} for 12 observed levels by using 11 parameters, and 8.9 cm^{-1} for 32 observed levels by using 13 parameters. These results are consistent with similar studies of rare earth ions doped in the $LaCl_3$ and LaF_3 crystals. Most of the calculated Zeeman splitting factors (g value) parallel to the principal axis of the crystals also are in fairly good agreement with the experimental values. Some discussion is given as to the effect of configuration interactions, the accuracy of wave functions obtained and the discrepancy between some of the calculated g values and the observed ones.

Most of early studies regarding the energy calculation of rare earth crystals were carried out by fitting both the intermediate coupling parameters (the Slater integrals F_k and spin-orbit coupling constant ζ) and the crystal-field parameters B_q^k to observed energy levels. Recently it has been recognized that the configuration interaction (CI) effects characteristic of the "free ion" levels (the center of gravity of a multiplet) of rare earth crystals is more important than those arising from the crystal-field potential. Some attempts[1-3] have been made to identify such effective interactions operating within $4f^N$ configuration that reproduce the observed electronic structure of crystals. The basic theory consists of simultaneously diagonalizing (J-mixing) both ion and crystal parts of an extended Hamiltonian matrix which involves several additional parameters introduced from the second-order perturbation theory. In recent analyses, the least-squares fits of 20 parameters to over 100 observed levels resulted in a mean error of less than 10 cm^{-1} for the energy levels of rare earth ions doped into $LaCl_3$[4-6] and that of about 20 cm^{-1} or less for the energy levels of rare earth ions doped into LaF_3.[7]

In this paper, the energy levels of praseodymium ethyl sulfate, $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$ (Pr(ES)), magnesium praseodymium nitrate, $Mg_3Pr_2(NO_3)_{12} \cdot 24H_2O$ (Pr(DN)), and thulium ethyl sulfate, $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$ (Tm(ES)), are calculated by the aforementioned extended Hamiltonian. The purpose of the present calculations is to determine the wavefunctions giving good agreement of both the calculated energy levels and Zeeman splitting factors (*i.e.*, g values) with the observed ones.

Calculational Procedure

Hamiltonian Structure. The theoretical formulation of electronic structures of rare earths by the tensor operator method has first been developed by Racah[8] and several authors have expanded this method to introduce the configuration mixing effects by using the second-order perturbation theory. Rajnak and Wybourne gave a detailed treatment for the second-order effect of electrostatic interactions[9] and also investigated the combined effects between spin-orbit and electrostatic interactions.[10] Furthermore Rajnak[3] discussed the relative roles of various mechanisms of CI by the application of this theory to the $4f^3$ configuration of the Pr^{2+} ion. Judd *et al.*[11,12] independently treated the intra-atomic magnetic interactions due to relativistic correction, and introduced several new parameters for spin-other-orbit interactions and electrostatically correlated spin-orbit interactions as main effects of these magnetic interactions. Here, an extended Hamiltonian on the basis of such refined tensorial method will briefly be given, especially for the second-order perturbation terms.

When we expand the wavefunction of a rare earth ion in crystals under the intermediate coupling scheme, a basis function is given as

$$|\Psi\rangle = \sum_i^N a_i \varphi_i | f^N; q, S, L, J, M\rangle, \tag{1}$$

where q is an additional quantum number introduced to distinguish the electronic states. The total Hamiltonian of $4f^N$ configuration can be written as

$$H = H_{\text{ion}} + H_{\text{cry}}, \tag{2}$$

where H_{ion} and H_{cry} are the ion and crystal-field parts of interactions respectively. H_{ion} for an N-electron system of rare earth ions with appreciable spin-orbit interaction may be given as

$$H_{\text{ion}} = \sum_i^N h_i + \sum_{i>j}^N e^2/r_{ij} + \sum_i^N \zeta_{4f}(\boldsymbol{s}_i \cdot \boldsymbol{l}_i), \tag{3}$$

where $$h_i = -(\hbar^2/2m)\Delta_i - Ze^2/r_i. \tag{4}$$

The Hamiltonian may be divided into $H_{\text{ion}} = H_0 + H_1$ such that

$$H_0 = \sum_i^N (h_i + v_i), \tag{5}$$

and

$$H_1 = -\sum_i^N v_i + \sum_{i>j}^N e^2/r_{ij} + \sum_i^N \zeta_{4f}(\boldsymbol{s}_i \cdot \boldsymbol{l}_i) = -V + G + A, \tag{6}$$

where v_i is an average potential that acts on the ith electron, while

$$V=\sum_i^N v_i,\quad G=\sum_{i>j}^N e^2/r_{ij},\quad \text{and}\quad \Lambda=\sum_i^N \zeta_{4f}(\boldsymbol{s}_i\cdot\boldsymbol{l}_i). \tag{7}$$

Within the first-order perturbation, the V term in Eq. 6 is purely radical and contributes energy shifts that are the same for all the levels belonging to a given configuration, while the G and Λ terms are different for different states of the same configuration. Hereafter, the perturbing terms, that are the same for all the levels belonging to a given configuration without affecting the energy-level structure of the configuration, are neglected because we are interested only in relative energy shift due to various interactions in the configuration. When a nonperturbing basis of $4f^N$ configuration and a perturbing basis belonging to a particular perturbing configuration are designated by $\langle\psi J|$ or $|\psi' J\rangle$ and $|mJ\rangle$ respectively, the perturbation energy E' due to the second-order perturbation theory may be expressed as

$$E'=\langle\psi J|H_1|\psi' J\rangle - \sum_m \langle\psi J|H_1|mJ\rangle\langle mJ|H_1|\psi' J\rangle/\Delta E_m. \tag{8}$$

The first-order perturbation energy in Eq. 8 is described in terms of the intermediate coupling parameters; *i.e.*, the Slater integrals $F_k(4f,4f)$ (or the equivalent E^k of Racah[8d]) and the spin-orbit coupling constant ζ_{4f}, and the reduction formula involving these parameters by the tensor method is given in a previous paper.[13]

The second-order perturbation energy in Eq. 8, exhibiting CI effects owing to the mixing levels from interacting configuration $|mJ\rangle$, consists of six distinct terms arising from substituting V, G, or Λ into the H_1 operators of matrix elements. The following three parts of them give rise to the dominant contribution:

$$-\sum_m \langle\psi J|G|mJ\rangle\langle mJ|G|\psi' J\rangle/\Delta E_m, \tag{9a}$$

$$-\sum_m \langle\psi J|\Lambda|mJ\rangle\langle mJ|\Lambda|\psi' J\rangle/\Delta E_m, \tag{9b}$$

$$-\sum_m \langle\psi J|G|mJ\rangle\langle mJ|\Lambda|\psi' J\rangle/\Delta E_m. \tag{9c}$$

Here, the terms, which may be absorbed as screening effects in the intermediate coupling parameters (F_k and ζ), are excluded. The tensorial reduction of Eq. 9a is given as[3,9]

$$\sum_{t\,\text{odd}} P(t)\langle\psi J|\sum_{i>j}(\boldsymbol{U}_i^{(t)}\cdot\boldsymbol{U}_j^{(t)})|\psi' J\rangle + \sum_{k,k'} X(kk',l')\,Y(kk',l'), \tag{10}$$

where the coefficient $X(kk',l')$ is given by

$$X(kk',l')=\sum_{k''\,\text{even}}(2k''+1)\begin{Bmatrix}k & k' & k''\\ l & l & l'\end{Bmatrix} \times\langle\psi\|\sum_{k\neq i\neq j}(\{\boldsymbol{U}_h^{(k)}\cdot\boldsymbol{U}_i^{(k'')}\}^{(k')}\cdot\boldsymbol{U}_j^{(k')})^{(0)}\|\psi'\rangle. \tag{11}$$

The first term in Eq. 10 is the same scalar two-body electrostatic interactions as those arising from the linear theory,[14,15] and, by using the properties of the Casimir operators,[16] is further simplified to the following expression,

$$\delta(\psi,\psi')[\alpha L(L+1)+\beta G(G_2)+\gamma G(R_7)], \tag{12}$$

where $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the group G_2 and R_7 used to classify the states of $4f^N$ configuration, and α, β, and γ are new parameters involving the radial factors and excitation energies. The second term in Eq. 10 represents effective three-body electrostatic interactions which are the nonlinear effects arising from interactions with $l^{N-1}l'$ configurations. The triple-tensor matrix elements in the coefficient $X(kk',l')$ expressing the angular dependence can be evaluated by a general expression of Rajnak.[3] $Y(kk',l')$ is a new parameter which depends on the radial integrals, excitation energies and the one-electron quantum numbers. Since there are ten distinct combinations of k, k', and k'' regarding the summation of the triple scalar product in Eq. 11 and the number of parameters is equal to the number of terms, then the number of independent $Y(kk',l')$ becomes to be ten. The combined reduction formula of Eqs. 9b and 9c by use of the algebra of tensor operators is given as

$$(-1)^{S'+L+J}\begin{Bmatrix}S' & L' & J\\ L & S & 1\end{Bmatrix}\langle qSL\|\boldsymbol{T}^{(11)}+\boldsymbol{t}^{(11)}\|q'S'L'\rangle. \tag{13}$$

In Eq. 13, the first term represents the spin-other-orbit magnetic interaction and is reduced to the form involving the Marvin integrals[17] M^k (k=0, 2, 4) as parameters, while the second term expresses the electrostatically correlated spin-orbit interaction and reduced to the form involving P^k(k=2, 4, 6) as pseudomagnetic parameters.[11]

The crystal-field potential H_{cry} in Eq. 2 may be expanded by the irreducible tensor $\boldsymbol{C}_q^{(k)}$ to give

$$H_{\text{cry}}=\sum_i^N\sum_k\sum_q B_q^k(\boldsymbol{C}_q^{(k)})_i, \tag{14}$$

where the summation including i is over all the electrons of the ion of interest and B_q^k is the crystal-field parameter to be determined from the experimental data. The reduction formula of the matrix element of H_{cry} is given in the previous paper.[13] The number of crystal-field parameters is restricted depending on the symmetry of the crystal-field potential and the maximum number of them does not exceed 27 even when an ion is at a site of no symmetry; the number is, in general, only a few for crystals with appropriate symmetry.

Within the above-mentioned framework for an effective Hamiltonian of $4f^N$ configuration, the total number of parameters necessary for energy-level fitting is less than 50; three Slater integrals F^k (k=2, 4, 6), one spin-orbit interaction ζ_{4f}, three two-body electrostatic interactions α, β, γ, ten three-body electrostatic interactions $Y(kk',l')$, three spin-other-orbit magnetic interactions M^k (k=0, 2, 4), three two-body pseudomagnetic configuration-mixing interactions P^k (k=2, 4, 6), and less than 27 crystal-field parameters B_q^k. In such semi-empirical approach, it will be seen later that the interaction energies as large as 10 cm^{-1} are taken into account for the energy fitting.

Application. The Pr^{3+} and Tm^{3+} ions have $4f^2$ and $4f^{12}$ configurations respectively. Since $4f^{12}$ configuration is complementary to $4f^2$, the Tm^{3+} ion has the same number and kind of levels as those of the Pr^{3+} ion, for which there are 13 different free-ion levels $|q,S,L,J\rangle$ under intermediate coupling. From the results of X-ray analyses, the space group and site symmetry at a rare earth ion are $P6_3/m$ (C_{6h}^2) and D_{3h} for ES,[18] and $R\bar{3}$ (C_{3i}^2) and C_{3v} for DN[19] respectively. The crystal fields of D_{3h} and C_{3v} symmetries are expanded as

TABLE 1. PARAMETERS AND ROOT MEAN SQUARE DEVIATIONS FOR $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$[a]

Parameter	Present work				Gruber[b]	Hüfner[c]
	I	II	III	IV		
F_2	310.93	310.53	310.17	309.76	307.4	
F_4	48.53	48.87	48.74	48.72	49.44	
F_6	4.857	4.866	4.856	4.856	5.138	
ζ_{4f}	749.8	739.1	736.2	737.3	727.9	
α	22.33	20.89	21.10	20.67		
β	−609	−644	−583	−536		
γ	453	636	643	612		
M^0		1.13	1.09	1.18		
P^2		34	54	70		
B_0^2			51.30	63.05	30.62	46.0
B_0^4			−745.3	−654.6	−706.6	−640
B_0^6			−877.2	−892.9	−780.2	−704
B_6^6			675.4	838.8	577.4	732
rms deviation						
For total 25 levels			7.8	10.1		
For 9 ion levels	25.1	5.0	4.4	5.2	212.5	
For 24 cryst. levels			7.0	9.1	7.7	10.8
$\|g\|$ value[d]			1.12	0.86	1.18	0.89

a) Energy units in cm^{-1}. The ion level and the rms deviation for crystal levels denote the center of gravity in a manifold and the rms deviation from the center respectively. b) Data from Ref. 23. Although he reported to be an average deviation of 3 cm^{-1} for total levels and that of 10.2 cm^{-1} for 9 ion levels with a slight change of the parameters, the details of calculations are not given explicitly. c) Data from Ref. 24. He obtained an average deviation of 5.9 cm^{-1} for 11 crystal levels. d) The absolute value of the ground state $^3H_4(\eta=\pm 2)$. The experimental g value is 0.775 (Ref. 25).

$$H_{cry}(D_{3h}) = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^6 C_0^{(6)} + B_6^6 (C_6^{(6)} + C_{-6}^{(6)}), \quad (15a)$$

$$H_{cry}(C_{3v}) = H_{cry}(D_{3h}) + B_3^4 (C_{-3}^{(4)} - C_3^{(4)}) + B_3^6 (C_{-3}^{(6)} - C_3^{(6)}). \quad (15b)$$

Each free-ion level under a crystal symmetry may be classified several irreducible representations designated by the crystal quantum number (η) following Hellwege;[20] *i.e.*, $\eta=0$, ± 1, ± 2, and 3 for ES, and $\eta=0$ and ± 1 for DN, where the levels with double signs are twofold degenerate. Any three-body interaction in Eq. 10 is not necessary to be taken into account in the case of f^2 configuration. For f^2 configuration, the reduced matrix elements of the magnetic interaction $\boldsymbol{T}^{(11)}$ and pseudomagnetic interaction $\boldsymbol{t}^{(11)}$ are already given in the explicit expressions involving M^k and P^k.[11] In practice, only M^0 and P^2 were freely varied and M^k and P^k were constrained to the following ratios proposed by Crosswhite *et al.*;[4] *i.e.*, $M^2=0.56M^0$, $M^4=0.38M^0$, and $P^4=0.75P^2$, $P^6=0.50P^2$. Other reduced matrix elements of various tensor operators with respect to f^N configuration are also tabulated by Nielson and Koster.[21] The procedure to determine the parameters by an iterative method is described in the previous paper.[13]

Once the eigenvectors are determined by diagonalizing the Hamiltonian, we can evaluate the parallel component of g values as

$$g_z = \langle\psi|\mu_z|\psi\rangle = \sum_i a_i^2 M g_i(qSLJ), \quad (16)$$

where μ_z is the z 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. The g value defined by Eq. 16 is half the Zeeman splitting in Lorentz units $\beta_e H$ (β_e=Bohr magneton). Then the total Zeeman splitting is expressed as $2g\beta_e H$.

Results and Discussion

The final parameters determined and the standard

TABLE 2. PARAMETERS AND ROOT MEAN SQUARE DEVIATIONS FOR $Mg_3Pr_2(NO_3)_{12} \cdot 24H_2O$[a]

Parameter	Present work	Judd[b]	Tinsley[c] in Nd (DN)
F_2	315.17		
F_4	51.38		
F_6	5.079		
ζ_{4f}	746.4		
α	22.81		
B_0^2	−158.9	−140	200
B_0^4	−0.7	−160	−166
B_3^4	−47.2	±140	±302
B_0^6	31.3	−800	1440
B_3^6	575.6	∓1800	±1760
B_6^6	−427.7	740	−1790
rms deviation			
For total levels	3.8(12)		
For ion levels	1.5(5)		
For cryst. levels	3.6(11)	6.1(8)	11.3(18)

a) See the footnote (a) in Table 1. The number of energy fitted is given in parentheses. b) Data from Ref. 29. c) Data from Ref. 30.

TABLE 3. PARAMETERS AND ROOT MEAN SQUARE DEVIATION FOR $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$[a]

Parameter	Present work	Gruber-Conway[b]	Wong-Richman[c]	Krupke-Gruber[d]
F_2	454.23	450.0		449.2
F_4	66.31	62.1		64.57
F_6	7.006	6.80		7.065
ζ_{4f}	2636.9	2700.0		2667.9
α	15.52			
β	−629.0			
γ	1962			
M^0	5.11			
P^2	1010.0			
B_0^2	277.1	26.0	259.6	270.6
B_0^4	−547.9	−640	−568.0	−570.8
B_0^6	−492.2	−512	−457.6	−460.8
B_6^6	394.8	316.0	455.6	450.7
rms deviation				
For total 32 levels	8.9			
For 10 ion levels	9.0	134.4[e]		58.4[e]
For 31 cryst. levels	4.7	25.6	8.2	7.1

a) See the footnote (a) in Table 1. b) Data from Ref. 35. c) Data from Ref. 33. They reported to be an average deviation of 5 cm^{-1} for 21 crystal levels. d) Data from Ref. 34. They reported that all the observed crystal levels were fitted within 4 cm^{-1}. e) The ion level $^1I_6$ is excluded. Both the deviation of this level by Gruber and Conway, and that by Krupke and Gruber are over 1000 cm^{-1}. Then the rms deviations for both cases are over 300 cm^{-1}, if the $^1I_6$ level is included.

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

Term	η	Energy level			$\lvert g \rvert$ (calcd)	Term	η	Energy level			$\lvert g \rvert$ (calcd)
		Exptl	Calcd	Diff				Exptl	Calcd	Diff	
$^3H_4$	±2	0	0	0	0.86	$^3F_4$	3		6720.4		
	3	12.2	9.6	−2.6			3		6802.4		
	±1		196.7		0.79		±2	6830.8	6821.4	−9.4	1.39
	±2		212.0		2.49		±1	6862.8	6861.2	−1.6	1.15
	3		245.6				0	6872.0	6857.4	−14.6	
	0		324.1				±2	6896.0	6904.4	8.4	3.73
$^3H_5$	3		2083.9			$^1G_4$	3		9478.4		
	±2		2127.5		0.04		0	9793.6	9791.4	−2.2	
	3		2211.2				±2	9811.0	9789.4	−21.6	0.98
	±1		2232.2		4.69		3		9808.3		
	±2		2250.8		2.02		±1	9862.8	9879.5	16.7	1.07
	±1		2290.4		0.59		±2		10052.7		1.18
	0		2333.2			$^1D_2$	0	16709.3	16715.4	6.1	
$^3H_6$	3		4087.3				±2	16857.7	16870.3	12.6	2.07
	±2		4183.2		2.04		±1	16955.0	16935.0	−20.0	1.03
	0		4319.9			$^3P_0$	0	20687.0	20691.3	4.3	
	0		4366.0			$^3P_1$	±1	21276.1	21260.0	−16.1	1.50
	±1		4373.3		3.78		0	21289.6	21279.3	−10.3	
	3		4373.6			$^1I_6$	0	21398.5	21391.8	−6.7	
	±2		4434.1		0.26		0	21407.6	21407.9	0.3	
	±1		4545.0		0.59		±1	21447.4	21449.3	1.9	0.28
	0		4555.6				0	21456.2	21440.7	−15.5	
$^3F_2$	±1		4988.0		0.44		±2		21542.8		1.00
	±2		5011.2		1.36		±1		21559.4		4.23
	0		5041.9				3		21601.2		
$^3F_3$	3		6309.9				±2		21674.7		2.98
	0	6310.4	6311.4	1.0			3		21700.2		
	±2	6330.7	6323.0	−7.7	2.14	$^3P_2$	0	22424.8	22425.6	0.8	
	±1	6382.6	6385.2	2.6	1.02		±2	22440.5	22448.5	8.0	2.90
	3		6425.9				±1	22447.6	22443.3	−4.3	1.42
						$^1S_0$	0		48995.8		

a) Energy units in cm^{-1}. Diff=Calcd−Exptl.

TABLE 5. EXPERIMENTAL AND CALCULATED VALUES OF THE ENERGY LEVELS AND g VALUES FOR $Mg_3Pr_2(NO_3)_{12}\cdot 24H_2O$[a)]

Term	η	Energy level			$\lvert g\rvert$ (calcd)
		Exptl	Calcd	Diff	
$^3H_4$	±1	0	0	0	0.67
	0	37.7	37.1	−0.6	
	0		48.8		
	±1	95.8	96.9	1.1	0.80
	±1		167.9		2.55
	0		174.5		
$^3H_5$	±1		2129.5		1.53
	0		2130.4		
	±1		2143.8		0.59
	0		2147.7		
	±1		2197.1		2.52
	0		2224.6		
	±1		2249.5		3.64
$^3H_6$	0		4242.6		
	±1		4269.3		0.66
	0		4270.9		
	±1		4300.1		0.33
	0		4328.8		
	±1		4366.5		2.94
	±1		4464.8		0.39
	0		4477.2		
	0		4550.6		
$^3F_2$	±1		4653.3		1.07
	±1		4684.7		0.31
	0		4689.8		
$^3F_2$	0		5978.2		
	±1		6008.7		0.54
	0		6054.4		
	0		6060.2		
	±1		6087.8		0.56
$^3F_4$	0		6668.3		
	±1		6679.3		3.79
	±1		6688.8		0.09
	0		6692.9		
	±1		6704.8		0.17
	0		6705.2		
$^1G_4$	0		9717.1		
	±1		9797.1		2.77
	±1		9815.0		0.93
	0		9956.3		
	0		9977.5		
	±1		10023.8		1.35
$^1D_2$	±1	16872.2	16868.2	−4.0	1.91
	±1	16920.0	16918.6	−1.4	0.88
	0	16933.6	16930.6	−3.0	
$^3P_0$	0	20845.9	20847.5	1.6	
$^3P_1$	0	21421.8	21417.3	−4.5	
	±1	21461.4	21463.8	2.4	1.50
$^1I_6$	0		21691.4		
	±1		21712.6		0.15
	±1		21742.4		0.30
	0		21753.4		
	0		21773.8		
	±1		21811.0		3.21
	±1		21851.6		4.76
	0		21909.6		
	0		21910.7		
$^3P_2$	±1	22630.1	22633.7	3.6	2.91
	±1	22693.3	22685.2	−8.1	1.45
	0	22695.8	22701.6	5.8	
$^1S_0$	0		50464.1		

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

TABLE 6. EXPERIMENTAL AND CALCULATED VALUES OF THE ENERGY LEVELS AND g VALUES FOR $Tm(C_2H_5SO_4)_3\cdot 9H_2O$[a)]

Term	η	Energy level			$\lvert g\rvert$ (calcd)
		Exptl	Calcd	Diff	
$^3H_6$	0	0	0	0	
	±1	32.2	35.5	3.3	0.67
	±2	111.5	122.3	10.8	1.13
	3	176.9	176.1	−0.8	
	±1	198.9	200.2	1.3	5.33
	0		226.3		
	0		230.8		
	±2	273.4	272.4	−1.0	3.46
	3	302.5	300.1	−2.4	
$^3F_4$	±2		5729.9		3.16
	±1		5779.7		1.14
	0		5799.2		
	±2		5809.7		0.87
	3		5842.1		
	3		5944.8		
$^3H_5$	0		8191.7		
	±1		8227.4		0.95
	±2		8298.6		1.40
	3		8348.2		
	±1		8363.8		5.08
	±2		8378.5		3.47
	3		8396.5		
$^3H_4$	0		12517.4		
	3	12585.8	12573.0	−12.8	
	±1	12627.0	12603.9	−23.1	0.95
	±2	12648.7	12636.8	−11.9	1.82
	3	12704.4	12707.9	3.5	
	±2	12763.3	12754.3	−9.0	0.07
$^3F_3$	3	14406.6	14407.2	0.6	
	±1	14466.0	14455.6	−10.4	1.08
	±2	14485.7	14484.4	−1.3	2.16
	3	14487.3	14488.2	0.9	
	0		14508.5		
$^3F_2$	±2	15078.8	15090.8	12.0	1.51
	±1	15106.1	15111.1	5.0	0.76
	0		15175.2		
$^1G_4$	±2	21170.6	21176.5	5.9	1.36
	±1	21194.0	21198.1	4.1	0.96
	0		21214.0		
	±2	21279.5	21282.4	2.9	0.56
	3	21343.5	21340.6	−2.9	
	3		21477.5		
$^1D_2$	±2	27906.6	27894.2	−12.4	2.28
	0		27961.4		
	±1	27977.1	27961.7	−15.4	1.14
$^1I_6$	3		34816.2		
	±2	34843.6	34850.9	7.3	0.89
	3	34870.0	34868.4	−1.6	
	±2	34899.7	34897.9	−1.8	1.12
	±1		34919.1		0.83
	0		34940.7		
	±1		35014.1		4.83
	0		35220.4		
	0		35228.1		
$^3P_0$	0	35436.9	35448.9	12.0	
$^3P_1$	0	36400.9	36390.4	−10.5	
	±1	36484.2	36473.5	−10.7	1.50
$^3P_2$	±2	38144.9	38158.5	13.6	2.55
	±1	38184.9	38196.0	11.1	1.28
	0		38344.6		
$^1S_0$	0		74880.2		

a) See the footnote (a) in Table 4.

deviations are given in Tables 1—3 for Pr(ES), Pr(DN) and Tm(ES) respectively, together with those obtained by other authors. Now, the root mean square (rms) deviation is defined as

$$\sigma = [\sum_i \Delta_i^2/N]^{1/2}, \quad (17)$$

where Δ_i is the difference between the observed and calculated values of the ith level, and N is the number of observed levels. The calculated numerical results are given in Tables 4—6 for Pr(ES), Pr(DN), and Tm(ES) respectively.

Energy Levels for Pr(ES). The energy levels of Pr(ES) have been investigated by several authors.[22-24] We have used 25 crystal levels assigned by experiments. As seen in Table 1, the inclusion of three two-body electrostatic interactions (case I) considerably reduces the rms deviation for 9 ion levels except the $^3H_5$, $^3H_6$, $^3F_2$, and $^1S_0$ levels from 213 to 25 cm^{-1}, when compared to the result without CI parameters by Gruber. Further improvement of the rms deviation of 20 cm^{-1} for ion levels is achieved by including one magnetic interaction M^0 and one pseudomagnetic interaction P^2 parameter (case II). This fact evidently exhibits that the CI effects arising from magnetic interactions as well as electrostatic interactions play highly important role in giving ion levels. The fit for 25 observed levels by 13 adjustable parameters (case III) yields an rms deviation of 7.8 cm^{-1}. This deviation is the same order of magnitude as that in rare earth crystals.[4-7] The parameter values in case IV are determined so as to fit both the calculated energy levels and the g value of the ground state with the observed values. Although the rms deviation of 10 cm^{-1} for all the 25 levels in case IV is slightly larger than that in case III, the former g value is only 10% larger than the value (=0.775)[25] observed by paramagnetic resonance, whereas the latter g value is 1.45 times as large as the experimental one. As to the rms deviation for 24 crystal levels given in Table 4 (deviation from the center of gravity in a manifold) and the g value of the ground state, the results in cases III and IV is rather similar to those by Gruber and by Hüfner respectively. It is easily supposed that this fact arises from the difference of the crystal-field parameters B_q^k used.

In order to make this point further clear, the main terms of the eigenvectors for the ground state, $^3H_4$ ($\eta=\pm2$), are given in Table 7, together with the ground state eigenvector determined only within the ground state manifold to fit the experimental g value by Abragam and Bleaney.[26] As seen in Table 7, the coefficients of two dominant bases, $|^3H_4(M=2)>$ and $|^3H_4(M=-4)>$, in case IV are evidently different from those by Gruber: the ours are rather close to the coefficients estimated by Abragam and Bleaney. As seen in Eq. 16, a basis function with negative M makes the g value decrease against functions with positive M. Then a slight difference of coefficients between $|^3H_4(M=2)>$ and $|^3H_4(M=-4)>$ results in fairly large difference in calculated g values. The ground state manifold with $J=4$ is split into six crystal levels owing to the D_{3h} crystal symmetry; one $\eta=0$ level, one $\eta=\pm1$ level, two $\eta=\pm2$ levels and two $\eta=3$ levels. Thus a level to be mixed predominantly in the ground state, $^3H_4(\eta=\pm2)$, should be the other $\eta=\pm2$ level in the same manifold because the lowest $^3H_4$ ion level is separated far away from other ion levels. The mixing between two crystal levels with $\eta=\pm2$ in the ground state manifold is taken into account reasonably in case IV by fitting to the observed g value of the ground state, but this mixing is not taken in other energy fits, because there is no experimental value of this level to be available. Therefore, the crystal-field parameters in case IV is considered to be more reliable than those in other cases, even though the result in case IV is not so good as that in case III. In determination of a set of crystal-field parameters, the information of the experimental levels as many as possible within a given manifold is considered to be substantially more important than performing complete J-mixing. Furthermore it is dangerous to conclude simply that in energy-level fitting by restricted experimental data the wavefunction giving better rms deviation is immediately more accurate wavefunction.

Energy Levels for Pr(DN). From the spectral analysis of Pr(DN) by Hellwege and Hellwege,[27] 12 levels of 61 crystal levels and 5 levels of 13 ion levels have only been established experimentally.

Before a definitive X-ray diffraction analysis of Ce(DN),[19] Judd[28] developed a theory for the effect of the crystalline electric field on rare earth double nitrates. The crystal field potential may be regarded as having two components; the first is a dominating potential corresponding to icosahedral symmetry and the second is a weaker residual C_{3v} symmetry potential. In pure icosahedral symmetry,

$$B_0^2 = B_0^4 = B_3^4 = 0, \quad B_3^6 = \pm 1.5275 B_0^6,$$
$$\text{and} \quad B_6^6 = -0.9211 B_0^6. \quad (18)$$

Using this icosahedral approximation, Judd[29] estimated the crystal parameters of Pr(DN) with the rms deviation of 6.1 cm^{-1} for 8 crystal levels, and Tinsley[30] obtained the rms deviation of 11.3 cm^{-1} for 18 crystal levels of Nd(DN) (Table 2). The present calculation yields the rms deviation of 1.5 cm^{-1} for 5 ion levels and that of

Table 7. Coefficients of the eigenvectors for the ground state $^3H_4(\eta=\pm2)$ of $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$[a]

Author	$\|^1G_4(2)>$	$\|^1G_4(-4)>$	$\|^3H_4(2)>$	$\|^3H_4(-4)>$	$\|^3H_5(-4)>$	$\|g\|$ value
Present work	0.1408	−0.0553	0.9077	−0.3835	0.0612	0.86
Gruber[b]	0.1429	−0.0405	0.9430	−0.2899	0.0469	1.18
Abragam-Bleaney[c]			0.9135	−0.4067		0.775

a) The basis functions with coefficients over 0.05 only are given. Values in parentheses are the z component of total angular momentum J. b) Data from Ref. 23. c) Data from Ref. 26.

3.6 cm^{-1} for 11 crystal levels. The result exhibits unexpectedly good agreement between the calculated and experimental values, but does not satisfy the relation predicted by Judd (Eq. 18).

According to the crystal structure of Ce(DN),[19] 12 oxygen atoms being the nearest-neighbors of the Ce atom must be moved distances of the order of 0.5 Å to make the icosahedron regular and most of 20 triangle on the surface of an icosahedron are also considerably irregular. Therefore the icosahedral model for rare earth double nitrates should be allowed only as the first approximation. Thus the three crystal parameters, B_0^2, B_0^4, and B_3^4, might be not necessary to be small compared to the six-order parameters. However, it is not adequate to conclude immediately that the crystal parameters obtained by us are reasonable because of the lack of experimental values to be fitted.

Energy Levels for Tm(ES). The observed energy levels have been reported by several authors[31-34] and some parameter analyses[33-35] have been carried out. Here, we have adopted the quantum numbers and wavenumbers by Johnsen,[31] and by Krupke and Gruber.[34] As seen in Table 3, when the present result for ion levels is compared to previous studies, the inclusion of CI parameters reduces the rms deviation of 58 or 134 cm^{-1} for the ion levels to 9 cm^{-1}. This remarkable improvement for Tm(ES) is the same degree as that for Pr(ES). For the assignment of ion levels with $J=4$, of which eigenvectors are given in Table 8, there is a substantial discrepancy between the present result and previous ones. The ion level at 5635 cm^{-1} and that at 12475 cm^{-1} are designated respectively to $^3F_4$ and $^3H_4$ unlike all previous assignments as far as the present parameters are appropriate.

TABLE 8. EIGENVECTORS OF THE ELECTRONIC TERMS WITH $J=4$ OF $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$

Energy (cm^{-1})	Coefficients of basis			Assignment
	$\|^3H_4\rangle$	$\|^1G_4\rangle$	$\|^3F_4\rangle$	
5635	−0.2799	0.5348	0.7973	$^3F_4$
12475	0.7766	−0.3621	0.5155	$^3H_4$
21089	0.5644	0.7635	−0.3140	$^1G_4$

For crystal levels, our result yielding an rms deviation of 4.7 cm^{-1} improves fairly previous results[33-35] which were obtained only within a given manifold by using the first-order perturbation theory. This improvement might simply be considered to be due to complete J-mixing. However, it is seen by examining the present result in somewhat details as well as previous results of crystals with f^3 configuration[13,36] that the mixing of an ion level into other ion levels of different J through crystal field perturbation is still fairly small. This will be plausible when we consider that the energy separation between most of lower excited ion levels well established by experiments is of the order of 10^3—10^4 cm^{-1}, whilst the interaction energy due to crystal field perturbation is of the order of 10—100 cm^{-1} and do not exceed 300 cm^{-1} at most, although the admixing due to crystal fields are, in principle possible for the most part of levels with different J. Thus if all the crystal levels within a manifold with relatively large J value are known completely from the experiments, the crystal-field parameters determined only within this manifold may be fairly reliable. This fact is obviously seen in Er(ES),[13] in which the energy calculation by complete J-mixing does not bring any improvement of the rms deviation when compared to that by crystal-field parameters determined only from the ground state manifold, where all of 8 crystal levels are known by experiments.

From the above consideration, it is more important than a least-squares fit including complete J-mixing for determination of reliable crystal parameters that there exists at least one manifold with J value as large as possible, of which most of the crystal levels are settled by experiments.

TABLE 9. COMPARISON OF ABSOLUTE g VALUES

Level	Energy (cm^{-1})	Exptl $\|g\|$		Calcd $\|g\|$	
		Zeeman[a]	MCD[b]	Present	W-R[c]
Pr(ES)					
$^3H_4(\pm2)$	0	0.85 (0.775)	0.77	0.86	
$^1D_2(\pm2)$	16858	1.30	1.30	2.07	
(±1)	16955		1.09	1.03	
$^3P_1(\pm1)$	21276	1.39	1.61	1.50	
$^3P_2(\pm1)$	22448	1.58		1.42	
Pr(DN)					
$^3H_4(\pm1)$	0	0.72 (0.725)	0.79	0.67	
$^1D_2(\pm1)$	16872	1.67		1.91	
$(\pm1')$	16920	1.12		0.88	
$^3P_1(\pm1)$	21461	1.17	1.24	1.50	
Tm(ES)					
$^3H_6(\pm1)$	32	0.57[d]	1.11	0.67	0.55
$^3H_4(\pm2)$	12649	1.57		1.82	1.85
$(\pm2')$	12763	0.0		0.07	0.06
$^3F_3(\pm2)$	14486	1.88	1.45	2.16	2.17
$^3F_2(\pm2)$	15079	1.46	1.34	1.51	1.51
$^1G_4(\pm2)$	21171	1.80	1.89	1.36	1.52
$(\pm2')$	21280	0.0	0.11	0.56	0.40
$^1D_2(\pm2)$	27907		1.99	2.28	2.27
(±1)	27977		1.23	1.14	1.14
$^3P_1(\pm1)$	36484		1.48	1.50	

a) Values in parentheses are those from paramagnetic resonances. See Refs. 25 and 38 for Pr(ES) and Pr(DN) respectively. b) See Refs. 40 and 39 for Pr(ES) and Pr(DN), and Tm(ES) respectively. c) Values by Wong and Richman. See Ref. 33. d) The value that Wong and Richman (Ref. 33) recalculated using the datum of the Zeeman splitting obtained by Johnsen (Ref. 31). Johnsen reported for this g value to be 1.0 ± 0.2.

Estimate of g Values. The experimental g values of Pr(ES), Pr(DN), and Tm(ES) have been obtained by the Zeeman effects,[22,31,37] paramagnetic resonances,[25,38] and recently magnetic circular dichroisms (MCD).[39,40] The comparison of the calculating g values to these experimental values are tabulated in

Table 10. Summary of calculated g values for crystals with f^3 configuration[a)]

Crystal	No. of fitted level	rms dev. (cm^{-1})	No. of g with dev. over 35%
Nd(ES)[b)]	43	3.6	1(7)
Er(ES)[b)]	50	3.6	2(14)
Nd: $LaCl_3$[c)]	66	4.9	4(33)
Nd(DN)[d)]	18	10.9	12(34)

a) Values in parentheses are total number of calculated g values compared to the observed ones. b) Data from Ref. 13. c) Data from Ref. 36. d) Data from Ref. 30.

Table 9. The calculated g values except those of the $^1D_2(\eta=\pm 2)$ level in Pr(ES) and the $^1G_4(\eta=\pm 2')$ level in Tm(ES) are in good agreement within 30% with the experimental values. Similar situation is found in rare earth crystals with f^3 configuration as shown in Table 10, where some of g values are very different from the experimental values.

It is not easy to find why only some of calculate g values involve large discrepancy although almost all of those are fairly consistent with experimental values. Undoubtedly, one of the origins may still be in experimental errors due to the misclassification of observed crystal levels, the broadening of the Zeeman lines and the overlap of the MCD curves. The other may arise from the inadequacy of crystal parameters due to the lack of energy levels to be available as pointed out in Pr(ES). Obviously the theoretical evaluation of some physical quantities, such as g value, exclusively depends on the accuracy of wavefunctions used. The present semiempirical procedure by the tensor method turns out to get a set of wavefunctions which are in good agreement with the average value of r^{-1}, because the main part of the Hamiltonian consists of the Coulomb interactions and the radial integrals as parameters contained in the Hamiltonian are determined to reproduce the experimental energy levels. On the other hand, the evaluation of g value given in Eq. 16 comes to estimate the average value of r^0; *i.e.*, a sum of overlap-type integrals. A basis $|J,M>$ under intermediate coupling is transformed to $|J',M'>$ on operation of the magnetic dipole moment operator $\mu=\beta_e(L+2S)$, where J' and M' are respectively equal to J and M or different from J and M by one unit, since both orbital and spin operators are a tensor operator of rank one. Consequently, the operation of magnetic dipole moment on a ket vector is to yield a new ket vector, then the average value of the magnetic dipole moment is reduced to a sum of several overlap-type integrals. Thus the wavefunction being fitted to energy levels may be better charge density in the region of r^{-1}, but it is not assured to give also better charge density in the region of r^0. In principle, exact wave function should give exact value for physical quantities as well as for the energy. However, an approximate wave function which is better regarding the energy levels does not necessarily yield better physical quantities. Such circumstances are, of course, manifested already for theoretical estimate of physical quantities of a number of simple molecules.[41] Such disadvantage is considered to be impossible to avoid in semiempirical method depending on solely energy level fitting. In practical purpose, it will be desirable that there are fairly amount of experimental energy levels to be available. However, it might be stated that the calculated g value can, at least, be taken as a reference when no experimental value is available.

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