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Electronic Spectrum and Energy Levels of Gd^{3+} in LaF_3

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The optical-absorption and fluorescence spectra of Gd^{3+} in crystals of LaF_3, pure GdF_3, and mixed crystals of 50% CaF_2 : 50% GdF_3 are given. Absorption has been observed in all the states of the ${}^6P$, ${}^6I$, and ${}^6D$ multiplets, with the exception of ${}^6D_{1/2}$ state. Fluorescence from the components of the ${}^6P_{7/2}$ state has been observed. A least-squares fit of 14 barycenters, with the inclusion of configuration interactions, gave a mean error of 43 cm^{-1} between the calculated and experimental barycenters, with the parameter values $F_2=419.1$ cm^{-1}, $F_4=56.54$ cm^{-1}, $F_6=6.006$ cm^{-1}, $\zeta_{4f}=1486$ cm^{-1}, and $\alpha=21.78$ cm^{-1}. With the inclusion of spin-other-orbit and spin-spin effects, the mean error was reduced to 32 cm^{-1}. The intermediate-coupling free-ion calculation was carried out assuming nonhydrogenic ratios of the Slater parameters.

INTRODUCTION

TRIVALENT gadolinium belongs to the $4f^7$ configuration and consists of 119 multiplets which, through the spin-orbit interaction, give rise to 327 *SLJ* states involving octet, sextet, quartet, and doublet states. According to Hund's rule, the ground state of Gd^{3+} is ${}^8S_{7/2}$, which, being an S state, cannot be split in first order by crystalline fields. From electron spin resonance studies of Gd^{3+} in various salts,[1–7] one may conclude that the over-all crystal field splitting of the ground level in zero magnetic field is small and of the order of 0.3 cm^{-1}. The fact that ${}^8S_{7/2}$ is the ground state, leads one to anticipate that the gadolinium ion has a simpler absorption or fluorescence spectrum than the other trivalent rare earths in that the positions of the observed lines will effectively be an energy level diagram of the ion. Most lines occur in the ultraviolet region, the lowest absorption lines being observed at approximately 3100 Å for all salts previously studied. Also, depending on the host lattice, the detection of the excited states around 45 000 cm^{-1} may be hampered by the absorption of the radiation by the host crystal.

Among the trivalent rare earths, Gd^{3+} is unique in that it possesses distinctive characteristic properties associated with a half-filled shell of equivalent $4f$ electrons. These distinctive features allow separation of the states of the f^7 configuration into two classes.[8] The states with seniority $v=7$ or $v=3$ belong to class I, while those with seniority $v=5$ or $v=1$ belong to class II. No matrix elements of the spin-orbit and crystal field interactions exist among states of the same class, whereas the matrix elements of the Coulombic, orbit-orbit, and spin-spin interactions are nonvanishing only for states of the same class. The tabulated states[9] in terms of the Racah quantum numbers *vWSUL* indicate that the ${}^8S$, ${}^6D$, ${}^6G$, and ${}^6I$ states belong to class I, while the ${}^6F$, ${}^6P$, and ${}^6H$ states belong to class II.

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The total observed splitting of approximately 1200, 800, and 1300 cm^{-1}, respectively, for the ^6P, ^6I, and ^6D multiplets for Gd^{3+} in crystals of GdCl$_3\cdot$6H$_2$O, GdBr$_3\cdot$6H$_2$O, LaCl$_3$, and LaF$_3$ indicates the existence of a strong spin-orbit coupling between states belonging to different classes. Therefore, to obtain accurate spin-orbit and Slater parameters for Gd^{3+} which reflect the correct energy and order in which the levels of a multiplet occur, it is desirable to perform the calculation by diagonalizing the Hamiltonian, consisting of the coulombic and spin-orbit interactions including all the states of the f^7 configuration.

During the 1930's, detailed absorption spectra of several gadolinium salts were observed by Freed and Spedding[10] and by Spedding and Nutting.[11] Together with the Zeeman study of GdCl$_3\cdot$6H$_2$O by Spedding,[12] they provided detailed information of the spectra of Gd^{3+}. The first assignments were made by Dieke and Leopold[13] of the levels which belong to the $^6P_{7/2}$, $^6P_{5/2}$, and $^6I_{7/2}$ states for GdCl$_3\cdot$6H$_2$O, and by Cook and Dieke[14] of the $^6P_{7/2}$, $^6P_{5/2}$, and $^6P_{3/2}$ states for the crystals of gadolinium acetate$\cdot$4H$_2$O and Gd$_2$(SO$_4$)$\cdot$8H$_2$O. The experimentally determined levels of the ^6P multiplet formed the basis for several theoretical investigations by Lacroix[15] and by Runciman.[16] In these calculations the $4f$ wave functions are assumed to be hydrogenic, whereas values for ζ and F_2 were selected either from interpolation between published results for Eu^{3+} and Tb^{3+} or by arbitrarily fixing the ratio of ζ/F_2. Hellwege, Hüfner, and Schmidt[17] reinvestigated the absorption spectrum of GdCl$_3\cdot$6H$_2$O and reported on the ^6P, ^6I, and ^6D multiplets. Using interpolated values for the Slater parameters from the available data from other trivalent lanthanides, and a value of $\zeta=1480$ cm^{-1}, which gave the correct multiplet splitting, Wybourne[18] calculated the spectrum of Gd^{3+}. Although the calculated multiplet splittings agreed with the data observed by Hellwege *et al.*,[17] the positions of the barycenters of the multiplets suggested the coulombic parameters needed further adjustment.

The inclusion of configuration interaction effects, especially for excited-state energy levels, has been shown to reduce significantly the deviations of the calculated barycenters of the multiplets from their experimental observed values.[19–24] For an f^N configuration, Rajnak and Wybourne[25] have shown that this interaction can be represented by an effective operator such that the diagonal matrix elements are given by

$$\alpha L(L+1)+\beta G(G_2)+\gamma G(R_7),$$

where α, β, and γ are interaction parameters and the values for $G(G_2)$ and $G(R_7)$ are tabulated.[9] From published analyses of trivalent rare earths including configuration interaction effects, one may conclude that a value of approximately 20 cm^{-1} is well founded for the parameter α.[26–29] However, no conclusive evidence is available for the magnitude or signs of the parameters β and γ.

Recently, Piksis, Dieke, and Crosswhite[28] analyzed the spectrum of LaCl$_3$:Gd^{3+}. Their free-ion calculation assumed hydrogenic ratios for the Slater parameters, also $\zeta=3.60F_2$, and an $\alpha L(L+1)$ configuration interaction term with $\alpha=23$ cm^{-1}.

In an attempt to improve the agreement between experiment and theory, more sophisticated interactions have been considered by Judd and co-workers.[29–31] An examination of the interaction effects of spin-spin (H_{ss}) and spin-other-orbit (H_{soo}) on the energy levels of the f^7-electron configuration, revealed typical shifts of the energy levels of about 10 cm^{-1} due to H_{ss} and 100 cm^{-1} due to H_{soo} interactions.

In this paper, we report the absorption and fluorescence spectra of Gd^{3+} in LaF$_3$ at liquid-helium and liquid-nitrogen temperatures in the range from 2000–3200 Å. The intermediate coupling free-ion energy levels have been calculated, including the effects of all the states of f^7 configuration, using 14 experimentally established barycenters which belong to the states of the ^8S, ^6P, ^6I, and ^6D multiplets. Because the observed transitions for Gd^{3+} lie above 32 000 cm^{-1}, it is most likely that the $4f^7$ configuration is perturbed by the $4f^55d^2$ configuration. A correction term $\alpha L(L+1)$ has been included in the calculation of the intermediate-coupling energy levels to account for the contribution of the odd-parity configuration. In the least-squares analysis the Slater, spin-orbit, and configuration interaction parameters were assumed to be freely varying.

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Magnetic effects due to H_{soo} and H_{ss} interactions on the spectrum of Gd^{3+} were also investigated.

EXPERIMENTAL PROCEDURE AND RESULTS

Spectra were obtained with single crystals of Gd^{3+}-doped LaF$_3$, pure GdF$_3$, and a mixed crystal containing 50% CaF$_2$: 50% GdF$_3$. The LaF$_3$: Gd crystal was procured from Optovac and was of excellent optical quality and free of strains. The pure GdF$_3$ and the mixed crystal of 50% CaF$_2$: 50% GdF$_3$ were prepared by Robinson of the Hughes Research Laboratories, Malibu, Calif. Data on the absorption and fluorescence spectra in the range from 2700 to 3200 Å were taken in fourth order with a 3.4-m Jarrell-Ash Ebert spectrograph having a dispersion of 1.2 Å/mm. Absorption data in the 2000–2500 Å range were obtained in first order by means of a 0.3-m McPherson ultraviolet monochromator equipped with a 2400 lines/mm grating, and also by means of a Bausch and Lomb 505 spectrophotometer. Tables I and II summarize the absorption and fluorescence data. The observed groups of lines are labeled $A \cdots O$ following Hellwege *et al.*[17] In Gd : LaF$_3$, transitions to the $^6P_{3/2}$ state and to the states belonging to the ^6D multiplet were not observed. These transitions, however, were measured in GdF$_3$ and in the 50% CaF$_2$: 50% GdF$_3$ crystals. Although the lines in the pure and mixed crystals were broad and diffuse as compared to the sharp line spectrum of LaF$_3$: Gd, no measurable differences were detected in the line positions for the well-defined groups in the different crystals.

TABLE I. Absorption spectrum of Gd^{3+} in LaF$_3$ at 4.2°K.

Upper level Stark component	Quantum state	Wavelength in air (Å)	Wave number in vacuum (cm^{-1})	Relative intensity	Experimental barycenter (cm^{-1})
A_1	$^6P_{7/2}$	3107.18	32 174.21	8	32 195.40
A_2		3106.26	32 183.75	10	
A_3		3104.81	32 198.70	9	
A_4		3102.29	32 224.95	5	
B_1	$^6P_{5/2}$	3050.73	32 769.54	8	32 789.10
B_2		3048.85	32 789.69	7	
B_3		3047.15	32 808.06	10	
C[a]	$^6P_{3/2}$	2996.5	33 363.0		33 363.0
D_1	$^6I_{7/2}$	2783.05	35 921.20	7	35 956.43
D_2		2781.33	35 943.42	6	
D_3		2779.52	35 966.82	10	
D_4		2777.40	35 994.27	8	
E_1	$^6I_{9/2}$	2756.02	36 273.49	4	36 294.00
E_2		2755.18	36 284.55	5	
E_3		2753.66	36 304.57	10	
E_4		2752.99	36 313.41	7	
F_1	$^6I_{17/2}$	2751.55	36 332.41	6	36 357.86
F_2		2750.97	36 340.07	8	
F_3		2750.56	36 345.49	10	
F_4		2750.15	36 350.91	8	
F_5		2749.21	36 363.33	5	
F_6		2748.66	36 370.61	7	
F_7		2748.21	36 376.57	3	
F_8		2747.69	36 383.45	4	
G_1	$^6I_{11/2}$	2735.21	36 549.45	6	36 578.79
G_2		2734.31	36 561.48	9	
G_3		2733.56	36 571.51	10	
G_4		2732.57	36 584.76	7	
G_5		2731.91	36 593.60	2	
G_6		2730.54	36 611.96	5	
H_1	$^6I_{13/2}$, $^6I_{15/2}$	2726.96	36 660.02	3	36 715.60
H_2		2726.27	36 669.29	3	
H_3		2725.63	36 677.90	4	
H_4		2724.83	36 688.67	6	
H_5		2724.02	36 699.58	7	
H_6		2723.02	36 713.06	5	
H_7		2722.68	36 717.64	8	
H_8		2722.33	36 722.36	10	
H_9		2721.55	36 732.89	9	
H_{10}		2721.23	36 737.21	6	
H_{11}		2720.18	36 751.39	8	
H_{12}		2719.40	36 761.93	7	
H_{13}		2718.74	36 770.85	7	
K[a]	$^6D_{9/2}$	2515.0	39 749.0	···	39 749.0[a]
M[a]	$^6D_{7/2}$	2451.5	40 779.0	···	40 779.0[a]
N[a]	$^6D_{3/2}$	2444.5	40 896.0	···	40 896.0[a]
O[a]	$^6D_{5/2}$	2433.0	41 089.0	···	41 089.0[a]

[a] Experimental barycenters were obtained from observed transitions in crystals of 100% GdF$_3$ and 50% GdF$_3$: 50% CaF$_2$.

TABLE II. Fluorescence spectrum of Gd^{3+} in LaF$_3$.

Upper level Stark component	Quantum state	Wavelength in air (Å) 77°K	4.2°K
A_1	$^6P_{7/2}$	3107.49	3107.21
A_2		3106.57	
A_3		3105.08	
A_4		3102.53	

In general, $J+\frac{1}{2}$ Stark components were identified in absorption, the exception being the group of very weak and diffuse lines which are observed around 2400 Å and which correspond to transitions terminating on the Stark components of the ^6D states. The Stark levels of the $^6I_{13/2}$ and $^6I_{15/2}$ states are mixed. Their calculated barycenters are separated by only 14 cm^{-1}. In their assignments, we have followed the interpretation of Piksis, Dieke, and Crosswhite,[28] and have placed the experimental barycenter of the $^6I_{15/2}$ state below that of $^6I_{13/2}$ state.

Strong absorption lines were observed at ~2000 Å. Because of their strength one can surmise that either these lines are due to the $4f \rightarrow 5d$ allowed electric dipole transitions or they can tentatively be assigned to the ^6G states of the f^7 configuration. The ^6G states were calculated to lie at 50 000 cm^{-1}.

In fluorescence, transitions originating from A_1 through A_4 were observed at liquid-nitrogen temperature. Only one very intense sharp line at 3107.21 Å was observed at liquid-helium temperature. The intensities denoted in Table I are estimated values and represent relative spectral intensities on a scale from 1 to 10 for lines within each group only. No structure due to the Stark components of the $^8S_{7/2}$ ground state was observed.

FREE-ION ENERGY CALCULATIONS

The diagonalization of the Coulombic and spin-orbit energy matrices with the inclusion of the configuration interaction term $\alpha L(L+1)$ was carried out with the

TABLE III. Gadolinium energy levels.

SLJ	Calc. energy[a] (cm^{-1})	Expt. energy (cm^{-1})	LS coupling, g value	Intermediate coupling, g value	SL composition (%)
$^8S_{7/2}$	0	0	2.002	1.994	97 ^8S, 3 ^6P
$^6P_{7/2}$	32 237	32 195	1.716	1.678	76 ^6P, 13 ^6D, 7 ^4D, 2 ^8S
$^6P_{5/2}$	32 814	32 789	1.888	1.840	83 ^6P, 14 ^6D, 2 ^4D
$^6P_{3/2}$	33 380	33 363	2.403	2.348	90 ^6P, 8 ^6D, 1 ^4S
$^6I_{7/2}$	35 887	35 956	0.443	0.462	92 ^6I, 7 ^4H
$^6I_{9/2}$	36 265	36 294	0.828	0.836	94 ^6I, 5 ^4H
$^6I_{17/2}$	36 507	36 358	1.295	1.290	96 ^6I, 4 ^4K
$^6I_{11/2}$	36 579	36 579	1.035	1.038	96 ^6I, 3 ^4H
$^6I_{15/2}$	36 790	36 691	1.240	1.237	97 ^6I, 1 ^4K
$^6I_{13/2}$	36 776	36 746	1.159	1.159	97 ^6I
$^6D_{9/2}$	39 805	39 749	1.557	1.543	93 ^6D, 3 ^6F, 3 ^4F
$^6D_{1/2}$	40 640	···	3.339	3.309	99 ^6D
$^6D_{7/2}$	40 807	40 779	1.589	1.588	80 ^6D, 12 ^6P, 3 ^6F, 1 ^4D
$^6D_{3/2}$	40 912	40 896	1.869	1.890	89 ^6D, 8 ^6P, 1 ^6F
$^6D_{5/2}$	41 076	41 089	1.659	1.672	81 ^6D, 14 ^6P, 3 ^6F, 1 ^4D
$^6G_{7/2}$	50 224	···	1.143	1.188	25 ^6G, 16 ^4D, 12 ^4F, 10 ^6F, 7 ^4G, 6 ^2F, 5 ^4H, 3 ^2G, 2 ^6P, 2 ^6D, 2 ^6H
$^6G_{5/2}$	50 996	···	0.857	1.043	40 ^6G, 17 ^4D, 16 ^6F, 2 ^6H, 2 ^4G, 1 ^6D
$^6G_{9/2}$	51 296	···	1.274	1.304	56 ^6G, 27 ^6F, 4 ^6H, 3 ^6D, 2 ^4G, 2 ^4H
$^6G_{11/2}$	51 373	···	1.344	1.367	53 ^6G, 35 ^6F, 3 ^6H, 3 ^4G, 2 ^4H
$^6G_{3/2}$	51 901	···	−0.002	0.502	48 ^6G, 20 ^6F, 17 ^4D, 12 ^4F
$^6G_{13/2}$	53 171	···	1.386	1.366	87 ^6G, 7 ^4H, 4 ^6H

[a] Values of $F_2=419.1$, $F_4=56.54$, $F_6=6.006$, $\zeta_{4f}=1486$, and $\alpha=21.78$ cm^{-1} are found to give the best over-all agreement between the experimentally observed and calculated levels, with a rms deviation of 75 cm^{-1}. The rms deviation used here is defined as

$$\delta=[\Sigma\,(E_{\text{calc}}-E_{\text{expt}})^2/(n-k)]^{1/2},$$

where n corresponds to the number of barycenters, and k to the number of parameters used in the least-squares fit. The mean error is 43 cm^{-1}.

aid of an IBM 360 Model 50 computer. All the states of the f^7 configuration were used in the calculation. The spin-orbit and Coulombic matrices have previously been tabulated by Nielson and Koster.[32] The barycenters corresponding to the states of the ^8S, ^6P, ^6I, and ^6D multiplets were employed in the least-squares analysis to determine the Slater and spin-orbit parameters and the configuration parameter α. Using an iterative method, the freely varying parameters were determined by minimizing the sum of the squares of the deviations between the experimental and calculated barycenters. The computer program provided the energy levels, eigenvectors, and intermediate-coupling g values for the free-ion problem. Table III summarizes the results of the calculations, while Table IV shows in detail the eigenfunctions of the lowest levels. The calculated energy levels agreed with the experimental barycenters, with an average deviation of 43 cm^{-1}. The unobserved $^6D_{1/2}$ state is calculated at 40 640 cm^{-1}. The ^6G levels are determined to lie approximately 10 000 cm^{-1} above the ^6D states. The parameter values which are found to give the best over-all agreement between experiment and theory are tabulated in Table V. Included in Table V are previously determined free-ion parameters of Gd^{3+} obtained from data on different salts. From Table V we observe that a value of about 1480 cm^{-1} for ζ_{4f} is necessary in order to obtain agreement with the observed experimental multiplet splittings. This value of ζ_{4f} is smaller than the value of 1534 cm^{-1} obtained by using the empirical formula of ζ' by Judd and Lindgren,[33] or by interpolating between the known values for ζ_{4f} from Eu^{3+} and Tb^{3+} in other salts.[34] The calculated values of ζ_{4f} for the various salts, as summarized in Table V, are in excellent agreement. It appears that the multiplet splittings for Gd^{3+} are more insensitive to the particular host lattice in comparison with the splittings of the other trivalent rare-earth ions. This is evident from Table VI which shows the consistency of the magnitude of the multiplet splittings for Gd^{3+} in GdBr$_3$·6H$_2$O, GdCl$_3$·6H$_2$O, LaCl$_3$: Gd, and LaF$_3$: Gd. Using the wave functions listed in Table IV, the calculated intermediate-coupling g value of 1.994 is larger than the value of 1.990±0.001 determined by Jones, Baker, and Pope[5] for the $^8S_{7/2}$ state in LaF$_3$. Simi-

TABLE IV. Eigenfunctions of the lowest levels (including all coefficients greater than 0.100).

$^8S_{7/2}$	$0.986\,^8S+0.163\,^6P$
$^6P_{7/2}$	$0.871\,^6P-0.155\,^8S-0.356\,^6D+0.184(111)^{\text{a}}(20)\,^4D$ $+0.198(220)(22)\,^4D$
$^6P_{5/2}$	$0.913\,^6P-0.368\,^6D+0.104(111)(20)\,^4D$ $+0.111(220)(22)\,^4D$
$^6P_{3/2}$	$0.949\,^6P-0.278\,^6D-0.107(220)(22)\,^4S$
$^6I_{7/2}$	$0.961\,^6I+0.196(211)(21)\,^4H+0.166(211)(30)\,^4H$
$^6I_{9/2}$	$0.972\,^6I+0.162(211)(21)\,^4H+0.138(211)(30)\,^4H$
$^6I_{17/2}$	$0.980\,^6I-0.147(211)(21)\,^4K-0.130(211)(30)\,^4K$
$^6I_{11/2}$	$0.980\,^6I+0.124(211)(21)\,^4H+0.105(211)(30)\,^4H$
$^6I_{15/2}$	$0.986\,^6I-0.105(211)(21)\,^4K$
$^6I_{13/2}$	$0.985\,^6I$

[a] The numbers in parentheses correspond to the $W=(w_1, w_2, w_3)$ and $U=(u_1, u_2)$ quantum numbers.

TABLE V. Free-ion parameters for Gd^{3+} (cm^{-1}).

Host lattice	GdCl$_3$·6H$_2$O[a]	LaCl$_3$[b]	LaCl$_3$[c]	LaF$_3$
F_2	372.1	408.0	421.5	419.1
F_4	53.58	56.4	55.30	56.54
F_6	5.407	6.17	6.035	6.006
ζ_{4f}	1480	1470	1497	1486
α	···	[23][d]	[20]	21.78
M^0	···	···	1.71	1.20
M^2	···	···	[1.71]	[1.20]
M^4	···	···	[1.71]	[1.20]

[a] Parameters adopted by B. R. Wybourne to fit GdCl$_3$·6H$_2$O data (Ref. 18).
[b] The values correspond to the hydrogenic parameters of A. H. Piksis, G. H. Dieke, and H. M. Crosswhite (Ref. 28).
[c] Nonhydrogenic parameters of B. R. Judd, H. M. Crosswhite, and H. Crosswhite (Ref. 29).
[d] The square brackets indicate parameters which were fixed in the calculation.

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lar results were obtained by Wybourne,[18] who concluded that the correct explanation of the observed $^8S_{7/2}$ splitting and g value must involve the detailed interaction of the ligands with the gadolinium ion.

Recently, the importance of the spin–other-orbit and spin-spin interactions between f electrons has been demonstrated.[29–31] For an f^N configuration, the inclusion of the H_{soo} and H_{ss} effects introduces in the analysis new parameters M^k ($k=0,2,4$) and P^k ($k=2,4,6$) to be determined. Since only four multiplets are observed, the meager data require some simplifying assumptions in order to keep the calculation physically meaningful. As suggested by Judd, Crosswhite, and Crosswhite,[29] we will compromise and impose the condition $M^0=M^2=M^4$ and $P^k=0$. The M^k are the radial integrals of Marvin,[35] which are proportional to

$$\langle (nl)^2 | (r_<^k / r_>^{k+3}) | (nl)^2 \rangle ,$$

and appear in the expressions for H_{soo} and H_{ss}. Since these interactions are of the order of 100 cm^{-1}, it is appropriate to calculate their effects by first-order perturbation theory and by choosing the value of M^0 for which the calculated energy levels agree with experiment. Table VII summarizes the results. The value of 1.20 was found to give the best agreement with the experimental data, reducing the mean error to 32 cm^{-1}.

TABLE VI. ^6P, ^6I, and ^6D multiplet splitting for Gd^{3+} in various salts (cm^{-1}).

Magnitude of multiplet splitting	$GdBr_3 \cdot 6H_2O$[a]	$GdCl_3 \cdot 6H_2O$[b]	$LaCl_3 : Gd$[c]	$LaF_3 : Gd$
$^6P_{7/2}$–$^6P_{5/2}$	592	595	597	594
$^6P_{5/2}$–$^6P_{3/2}$	···	572	572	574
$^6I_{7/2}$–$^6I_{9/2}$	342	344	345	338
$^6I_{9/2}$–$^6I_{17/2}$	···	66	51	64
$^6I_{17/2}$–$^6I_{11/2}$	···	216	226	221
$^6I_{11/2}$–$^6I_{15/2}$	···	105	116	112
$^6I_{15/2}$–$^6I_{13/2}$	···	60	36	55
$^6D_{9/2}$–$^6D_{7/2}$	1020	1012	1031	1030
$^6D_{7/2}$–$^6D_{5/2}$	319	327	···	318

[a] Values obtained from data by G. C. Nutting and F. H. Spedding (Ref. 11).
[b] Data obtained from K. H. Hellwege, S. Hüfner, and H. Schmidt (Ref. 17).
[c] Data obtained from A. H. Piksis, G. H. Dieke, and H. M. Crosswhite (Ref. 28).

TABLE VII. Energy levels of $LaF_3 : Gd$ with the inclusion of H_{soo} and H_{ss}.

SLJ	Experimental barycenters (cm^{-1})	Calculated levels including $F_2, F_4, F_6, \zeta, \alpha$	$M^0=1.71$	$M^0=1.20$
$^8S_{7/2}$	0	0	0	0
$^6P_{7/2}$	32 195	32 237	32 224	32 232
$^6P_{5/2}$	32 789	32 814	32 834	32 828
$^6P_{3/2}$	33 362	33 380	33 366	33 360
$^6I_{7/2}$	35 956	35 887	36 036	35 991
$^6I_{9/2}$	36 294	36 265	36 366	36 336
$^6I_{11/2}$	36 579	36 579	36 643	36 624
$^6I_{13/2}$	36 746	36 776	36 770	36 772
$^6I_{15/2}$	36 691	36 790	36 733	36 750
$^6I_{19/2}$	36 358	36 507	36 407	36 437
$^6D_{9/2}$	39 749	39 805	39 778	39 786
$^6D_{1/2}$	···	40 640	···	···
$^6D_{7/2}$	40 779	40 807	40 796	40 800
$^6D_{3/2}$	40 896	40 912	40 952	40 940
$^6D_{5/2}$	41 089	41 076	41 090	41 086
Mean error	···	43	38	32

These results are compared with the energy levels obtained with a value of $M^0=1.71$, obtained by Judd *et al.*[29] from the analysis of $LaCl_3 : Gd$.

In conclusion, the optical spectrum of $LaF_3 : Gd$ has been obtained in the 2000–3200 Å spectral range. The parameters obtained from the analysis agree with the values obtained by Judd *et al.*[29] A value of 1486 cm^{-1} for the spin-orbit radial integral is required for explaining the observed multiplet splittings. Since only the ^8S, ^6P, ^6I, and ^6D multiplets were observed, the number of parameters used in the analysis was minimized to ζ_{4f}, $F_{2,4,6}$, and α. The effects of the parameters β and γ were not investigated. Their general contribution would be to shift the ^6D and ^6I states equally by an amount $\frac{1}{6}\beta+\frac{2}{5}\gamma$ with respect to the states of the ^6P multiplet. Unless other excited multiplets are experimentally verified, it is difficult at present to assess the effects of the more sophisticated magnetic interactions as compared with the complete set of configuration interaction parameters α, β, and γ.

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[35] H. H. Marvin, Phys. Rev. 71, 102 (1947).