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Line Strengths for Gd^{3+} at a C_{4v} Site in SrF_2[†]

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Oscillator strengths of the transitions from ${}^8S_{7/2}$ to some of the ${}^6P$, ${}^6I$, and ${}^6D$ multiplets at a C_{4v} symmetry site in SrF_2 : Gd^{3+} have been measured experimentally and compared with calculations using the Ofelt–Judd theory. Calculations using crystal-field wave functions for the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ spectra showed that J mixing is negligible and, in agreement with Zeeman measurements, the transitions are predominantly magnetic dipole. The ${}^6I$ transitions are predominantly electric dipole and the intensities are in good agreement with theory. The line-strength parameters T_λ are 3.4 ± 0.1, 1.05 ± 1.05, and 12.2 ± 0.05 cm $\times 10^{10}$ for $\lambda = 2$, 4, and 6, respectively.

INTRODUCTION

The alkaline-earth fluorides doped with trivalent rare-earth ions offer a unique opportunity to test line-strength calculations. The cubic site possesses inversion symmetry and allows only magnetic dipole or electric quadrupole transitions. This site is formed when the rare earth, located at a divalent cation site, is charge compensated by a negative ion more than two lattice constants removed.[1] At a site of axial symmetry, which lacks inversion, the odd components in the multipole expansion of the crystal field introduce opposite parity into the states of f^n, and electric dipole transitions may occur.

Thus the magnetic dipole strength can be studied independently of the combined electric and magnetic dipole transitions. An analysis of the ${}^6P$ transitions for the cubic site observed in CaF_2:Gd^{3+} has been reported.[2] In this paper the electric dipole contribution observed at a site of C_{4v} symmetry in SrF_2:Gd^{3+} is analyzed according to the Ofelt-Judd theory.[3,4]

OUTLINE OF CALCULATIONS

The calculations will be given in outline form here since the original paper by Judd[4] gives an excellent description of the theory. The contribution to the oscillator strength due to magnetic dipole transitions is given by

$$P_{\rm MD} = \frac{\pi h}{3mc}\,\frac{n\bar{\nu}}{8}\,\left|\left([{}^8S_{7/2}]\,\|\,L + g_s S\,\|\,[\alpha LSJ]'\right)\right|^2 .$$

The average energy of the transition is $\bar{\nu}$, n is the index of refraction, and the other constants have a value of 4.028×10^{-8} cm. The reduced-matrix elements are given for $\Delta J = 0$ by

$$(\alpha LSJ\,\|\,L + g_s S\,\|\,\alpha LSJ) = [J(J+1)]^{1/2} g \ ,$$

where g is the Landé g value given by the formula

$$g = (g_s - 1)\,\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} + 1 \ .$$

The gyromagnetic ratio of the electron, g_s, is 2.00327. For $\Delta J = -1$,

$$(\alpha LS, J|\,|L+g_sS|\,|\alpha LS, J-1) = (g_s-1)\left[\frac{(S+L+J+1)(J+L-S)(J+S-L)(S+L-J+1)}{4J}\right]^{1/2} ,$$

with an analogous expression for $\Delta J = 1$. The ΔJ selection rules obtained from the use of free-ion state vectors are closely obeyed in the cubic site spectra.[2]

The electric quadrupole contribution is about 1% of the MD portion for the ^6P levels studied. This contribution is given by

$$P_{EQ} = \tfrac{1}{8}\bar{\nu}^3 \chi_{EQ} T_2' |([^8S_{7/2}]|\,|U^{(2)}|\,|[\alpha LSJ])|^2 ,$$

where

$$\chi_{EQ} = \tfrac{1}{9}[n(n^2+2)^2] .$$

T_2' is about 9.17×10^{-21} cm^3 for Gd^{3+} if Freeman and Watson's[5] $(f^7|\,|r^2|\,|f^7)$ integrals are used. The reduced-matrix element, which also enters into the electric dipole calculation, will now be defined.

The electric dipole contribution is given by

$$P_{ED} = \frac{\bar{\nu}}{8}\frac{(n^2+2)^2}{9n} \times \sum_{\lambda=2,4,6} T_\lambda |([^8S_{7/2}]|\,|U^{(\lambda)}|\,|[\alpha LSJ])|^2 .$$

The reduced-matrix elements are

$$([\alpha LSJ]|\,|U^{(\lambda)}|\,|[\alpha' L' SJ']) = (-1)^{S+L'+J+\lambda}[(J+1)(J'+1)]^{1/2} \times \begin{Bmatrix} J & J' & \lambda \\ L' & L & S \end{Bmatrix} (\alpha LS|\,|U^{(\lambda)}|\,|\alpha' L' S) .$$

The doubly-reduced-matrix elements are found in tables[6] or computed from sums over fractional percentage coefficients.[7]

The selection rules are conveyed in part by the curly brackets which denote a 6-j symbol.[6] In the case of f^7, all diagonal matrix elements in the Racah basis are zero.

The parameter is given by

$$T_\lambda = \frac{8\pi^2 m}{3h}(2\lambda+1)\sum_{k\ \mathrm{odd}}(2k+1)A^k\,\Xi(k,\lambda) ,$$

where the dependence on odd terms in the multipole field expansion is

$$A^k = \sum_{|q|\lesssim k} |A_q^k|^2/(2k+1)$$

and

$$\Xi(k,\lambda) = 2\sum_{n'l'}(2l+1)(2l'+1)(-1)^{l+l'}\begin{pmatrix} 1 & \lambda & k \\ l & l' & l \end{pmatrix} \times \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}\frac{(nl|\,|r|\,|n'l)(nl|\,|r^k|\,|n'l)}{\Delta E_{nl,n'l'}}$$

The large curved brackets are 3-j symbols.[6] The parameter T_λ is usually found by fitting to experimental data. It may also be investigated from first principles.[8]

For crystal-field states described by linear combinations of the J_z quantum numbers, the polarization dependence is given by

$$P_{ED}^{\rho} = \frac{\bar{\nu}}{8}\frac{(n^2+2)^2}{9n}\sum_{q,k,\lambda}(2\lambda+1)(-1)^{\rho+q}\begin{pmatrix} 1 & \lambda & k \\ \rho & -(q+\rho) & q \end{pmatrix} \times \Xi(k,\lambda)|([\alpha LSJJ_z]|\,U_{\rho+q}^{(\lambda)}|\,[\alpha LSJJ_z]')|^2 .$$

When summed over the quantum numbers J_z and J_z' for the excited and ground multiplets and over all polarizations the results given above are obtained.

The matrix elements required to compute the line strengths are given in Table I. These values were calculated from the free-ion vectors obtained by diagonalizing the Hamiltonian due to Judd *et al.*[9] using the complete set of the 119 Racah states as a basis.

The effects of crystal-field J mixing were investigated for cubic[10] and C_{4v} symmetry.[11] In a site of cubic symmetry the transitions are purely magnetic dipole and require no adjustable parameters. Using the crystal-field state vectors of Ref. 11 the total $^6P_{7/2}$ and $^6P_{5/2}$ oscillator strengths are 6.41 and 3.53×10^{-8}, respectively. The values computed in the free-ion basis, neglecting crystal-field J mixing, are 6.35 and 3.58×10^{-8}, respectively.[2] The effects of J mixing on the ^6P multiplets in a cubic field are therefore negligible. Calculations for the C_{4v} basis showed similar results; the strengths are 6.59 and 3.62×10^{-8}, respectively. The agreement is within experimental error and the effects of crystal-field mixing are negligible for the C_{4v} site.

Even when transitions to individual crystal-field levels cannot be computed, the application of f sum rules to the LSJ multiplets allows the line-strength calculation to proceed with some reliability.

The calculated oscillator strength for the transitions between the $^8S_{7/2}$ ground states to all of the crystal-field levels belonging to a given $[\alpha LSJ]$ multiplet are

$$P_{\mathrm{calc}} = P_{ED} + P_{MD} + P_{EQ} ,$$

with P_{ED} found by applying a least-squares-fitting procedure to the determination of the T_λ parameter. This assumes that P_{MD} and P_{EQ} are equal to the calculated values. The quantity minimized is

TABLE I. Line-strength matrix elements for transitions from the intermediate-coupled $[^8S_{7/2}]$ ground state of Gd^{3+}.

Final state	$(L+2S)$	$(U^{(2)})$	$(U^{(4)})$	$(U^{(6)})$
$[^6P_{7/2}]$	−0.520	0.034	0.0023	0.00073
$[^6P_{5/2}]$	0.387	−0.022	0.00056	−0.00004
$[^6P_{3/2}]$	...	0.004	−0.00023	...
$[^6I_{7/2}]$	0.00709	0.00009	−0.0018	−0.066
$[^6I_{9/2}]$	0.00089	−0.0015	−0.0033	−0.105
$[^6I_{17/2}]$	...	...	...	−0.151
$[^6I_{11/2}]$	...	0.00009	−0.0037	−0.137
$[^6I_{15/2}]$	...	...	0.0012	−0.169
$[^6I_{13/2}]$	...	...	−0.0028	−0.160
$[^6D_{9/2}]$	0.0423	−0.078	−0.0088	0.0023
$[^6D_{1/2}]$	...	...	0.0006	...
$[^6D_{7/2}]$	0.148	−0.068	−0.0054	0.0005
$[^6D_{3/2}]$	...	−0.030	0.00057	...
$[^6D_{5/2}]$	0.107	−0.051	−0.0015	0.00006

$$\chi^2=\frac{1}{n-3}\sum_{i,j} w_i\{P_{\text{expt}}-P_{\text{MD}}-P_{\text{EQ}} - \sum_{\lambda=2,4,6}\frac{\bar{\nu}}{8}\,\chi_{\text{ED}}\,T_\lambda\left|\left([^8S_{7/2}]\left|\left|U^{(\lambda)}\right|\right|[\alpha LSJ]\right)\right|^2\}^2 .$$

The statistical weight is the reciprocal of the square of mean deviation of the integrated absorption-coefficient measurements. The results depend on how the experimental data are employed in the fitting process and will be given after a discussion of the measurements.

LINE-STRENGTH DATA

Integrated absorption coefficients for the multiplets $^6P_{7/2}$, $^6P_{5/2}$, $^6I_{7/2}$, ($^6I_{9/2}$ and $^6I_{17/2}$), ($^6I_{11/2}$, $^6I_{15/2}$, and $^6I_{13/2}$), $^6D_{9/2}$, and $^6D_{7/2}$ are given in Table II. The seven entries for each of four crystals in the table result from the fact that certain free-ion multiplets are so perturbed by the crystal-field interaction that they cannot be experimentally assigned to a particular J level. There are $J+\frac{1}{2}$ crystal-field levels per half-integral J multiplet at a site of axial symmetry, according to Kramers's theorem. The absorption values are the sums of these transitions to the crystal-field levels.

An interesting property of the C_{4v} sites in the fluorite lattice that has proven very useful is that the group-theoretical polarization selection rules predict no polarization effects. This result follows in part from the three mutually orthogonal nonequivalent directions that the charge compensating ion may define. If the incident radiation is polarized along one axis (and excites the π spectra), it is perpendicular to the other sites and excites their σ spectra. It is easy to show this for light propagating along one of the fourfold axes and is also true for an arbitrary orientation of the crystal and radiation. In effect, the three orthogonal axes perform a spatial integration over the radiation field. It is assumed in the group-theoretical argument that the π and σ spectra have equal intensities. In the case of Gd^{3+} in SrF_2 the weakly split ground state further reduces the polarization effects since the observed spectral lines are composed of unresolved transitions from each of the four ground levels. It was experimentally verified during earlier Zeeman studies that no detectable polarization effects exist in the absence of a magnetic field. The small ground-state splitting[12] (0.14 cm^{-1}) satisfies the spectroscopic stability criterion even at 77 °K and the data may be compared directly to theory.

The experimental details concerning these data are described elsewhere.[13] The mean deviations of the absorption coefficients are also found in Table II. The accuracy of these data is not solely a function of experimental spread. For the ^6I and ^6D multiplets there is some difficulty in assigning

TABLE II. Integrated absorption coefficient data for the C_{4v} site in SrF_2: Gd^{3+} from Ref. 13.

Concentration (mole/percent)		$\int\alpha(\nu)\,d\nu$ and $\Delta\alpha$ (cm^{-2})						
Nominal	Fitted	$^6P_{7/2}$	$^6P_{5/2}$	$^6I_{7/2}$	$^6I_{9/2,\,17/2}$	$^6I_{11/2,\,15/2,\,13/2}$	$^6D_{9/2}$	$^6D_{7/2}$
0.1	0.071	0.85	0.47	0.38	3.57	7.53	0.136	0.211
		±0.057	±0.042	±0.033	±0.23	±0.155	...[a]	...
0.23	0.176	2.12	1.14	0.96	7.64	18.07	0.417	0.772
		...	...	±0.004	±0.174	±0.392	...	...
0.36	0.233	2.8	1.52	1.36	9.94	23.76	0.471	0.762
		...	...	±0.06	±0.246	±0.173	...	...
0.5	0.242	2.92	1.56	1.45	11.16	24.8	0.43	0.771
		...	...	±0.07	±1.16	±0.94	...	...

[a] Adequate statistics were not developed for these entries. The mean deviations were assumed constant (equal statistical weights).

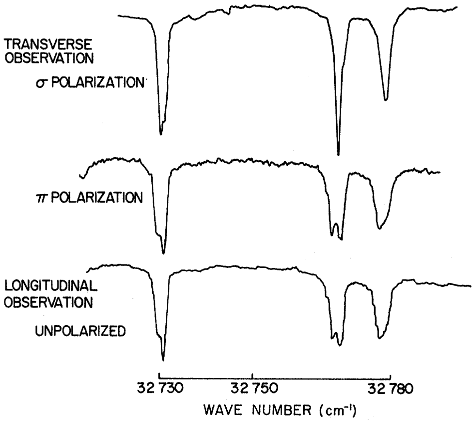

FIG. 1. Longitudinal and transverse Zeeman absorption spectra of the C_{4v} crystal-field $^6P_{5/2}$ multiplet of SrF$_2$: Gd^{3+}. The magnetic field is 6.1 kOe along the [001]. The sample is at 77 °K. In the transverse experiment, radiation is incident normal to the magnetic field and polarized with the electric vector perpendicular (σ) or parallel (π) to the field.

measured lines to the C_{4v} site spectra.

Errors in absolute measurement of integrated absorption were not discussed in Ref. 13 since only relative values were of interest. Uncertainties in measurement of plate contrast γ (5%), in the gradient of the densitometer wedge (5%), and in sample thickness (2%) contribute about 8% to the over-all absolute accuracy. In addition, the spread in measurement of area using a K and E planimeter contribute to the values given in Table II. The effect of the instrument slit width, less than $\frac{1}{4}$ of the linewidth, on area measurements was considered negligible[14] compared to those introduced by the integration process. Errors introduced by the slit are less than 2.5% in the worst case. It is possible that some lines (up to 4 or 5 in the ^6I multiplets) are incorrectly included in the C_{4v} spectra. The effect of such errors is assumed small in comparison to the mean deviations.

A comparison of unpolarized longitudinal Zeeman spectra in which the incident radiation (both electric and magnetic dipole) is oriented perpendicular to the magnetic field and may excite only the σ spectra and the transverse observations made with the electric vector polarized parallel, π, and perpendicular, σ, permits the determination of the multipolarity of the transitions. Since the transverse π spectra agree with the longitudinal observations, the transitions are predominantly magnetic dipole.[15] The Zeeman patterns are shown in Fig. 1. A quantitative estimate of the percentage of the transition which should be assigned magnetic dipole character may be inferred from these spectra. The lower limit of this value is about 90%.

The usual procedure in comparing measured line strength to calculations requires a knowledge of the number of ions contributing to the observed absorption. In this problem it is not enough to merely determine the total Gd^{3+} concentration in each sample. The number of ions in the tetragonal site is the quantity required. Spectrochemical analysis (total Gd^{3+}) is limited in accuracy to ± 10% for these samples and EPR measurements on the ratios of ions in specific sites could not be relied on to accurately determine the C_{4v} concentration. It is possible, however, to obtain a set of concentrations that fall within the experimental uncertainty by a least-squares analysis of the absorption coefficients.

The well-defined $^6P_{7/2}$ and $^6P_{5/2}$ transitions are used to fix the four concentrations and two oscillator strengths, a total of six parameters, by minimizing the residues with respect to the eight data (two transition groups in each of four samples). Additional details are given in Ref. 13. Although this procedure possesses only two degrees of freedom, it has the advantage of containing no spurious lines or excluding transitions that properly belong with the C_{4v} site spectrum.

Using the oscillator strengths obtained by assuming the concentrations that result from fitting only the ^6P data, the "experimental" values in Table III were found. These seven oscillator strengths were then used to obtain the T_λ by a numerical simplex minimization routine[16] based on the method of Nelder and Mead.[17] The parameters are found in Table IV. Figure 2 shows the results of the calculation.

It is possible to simultaneously fit all 28 data to obtain the best values of the four concentrations and three T_λ parameters. This procedure has 21 degrees of freedom but is derived from data containing unknown systematic errors and is not in-

TABLE III. Experimental oscillator strengths determined by a linear least-squares analysis of absorption data versus concentrations obtained from fitting the well-known $^6P_{7/2}$ and $^6P_{5/2}$ multiplet spectra at a site of C_{4v} symmetry.

Multiplets	Energy (cm^{-1})	Oscillator strength (× 10^8)
$^6P_{7/2}$	32 166.2	6.68 ± 0.01
$^6P_{5/2}$	32 758.4	3.60 ± 0.01
$^6I_{7/2}$	35 933.2	3.03 ± 0.02
$^6I_{9/2,\ 17/2}$	36 317	24.1 ± 0.5
$^6I_{11/2,\ 15/2,\ 17/2}$	36 641	56.8 ± 0.4
$^6D_{9/2}$	39 693.4	1.1 ± 0.1[a]
$^6D_{7/2}$	40 707.8	1.9 ± 0.2[a]

[a] Estimated values for the uncertainty. The other values are the standard error in the slopes obtained from the least-squares analysis.

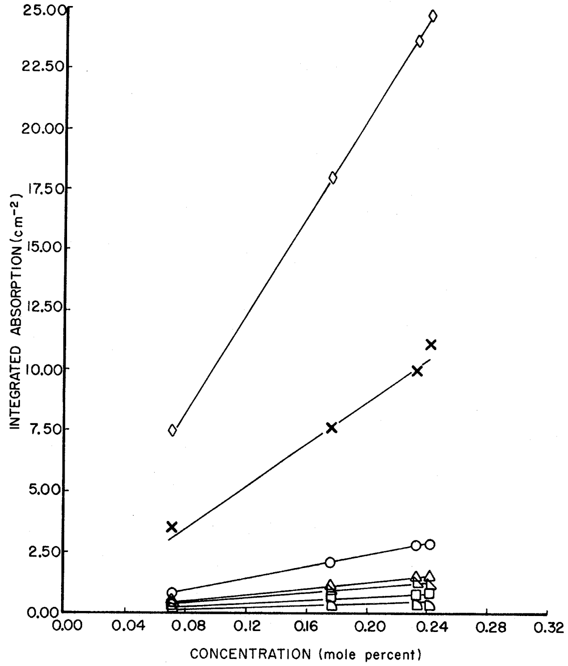

FIG. 2. Integrated absorption at 77 °K versus fitted C_{4v} site concentrations for the four samples and seven distinctly observed crystal-field multiplets. The slopes of the lines are proportional to the oscillator strengths and constrained to intercept the origin. In most cases the experimental uncertainty is within the symbols used to designate the data. From top to bottom the groups are $^6I_{11/2,\ 15/2,\ 13/2}$, $^6I_{9/2,\ 17/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^6I_{7/2}$, $^6D_{7/2}$, and $^6D_{9/2}$.

cluded here.

These procedures have one drawback—the parameters are poorly conditioned, i.e., the oscillator strengths are not independent of the concentrations. Several local minima have therefore been observed in the course of this work. The results shown in Fig. 3 are for the fit with smallest χ^2 which also agrees with the small electric dipole contribution observed for the ^6P multiplets.

DISCUSSION

The inclusion of crystal-field J mixing between the 15 lowest free-ion states showed that although a slight improvement was obtained, it is within experimental uncertainty to assume J mixing negligible. The use of sum rules allowed the successful application of the Ofelt-Judd theory for calculating electric dipole line strengths for the $4f$-$4f$ transitions.

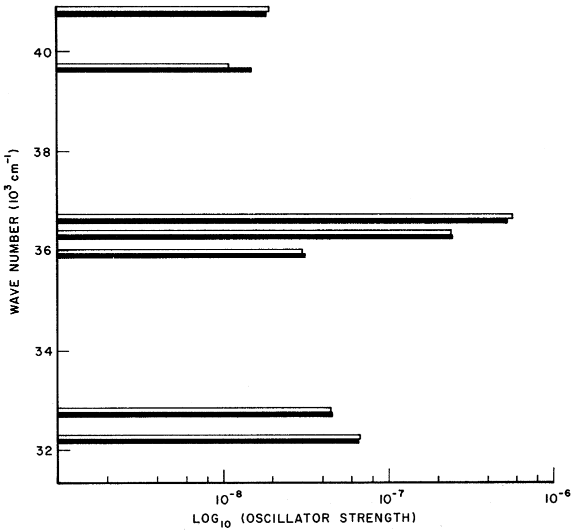

FIG. 3. Observed (open) and calculated (shaded) oscillator strengths for Gd^{3+} in SrF_2 at a C_{4v} site.

The electric dipole contribution to the $^6P_{7/2}$ and $^6P_{5/2}$ strengths is dominated by the second-rank reduced-matrix elements (see Table I). The ^6D spectra are also dominated by the second-rank terms; however, the $^6D_{1/2}$ transition, could it be observed, would uniquely define the parameter T_4 (in the approximation of negligible J mixing). The ^6I_J transitions are nearly pure electric dipole in origin and dominated by the sixth-rank terms and, therefore, afford an excellent test of the Ofelt-Judd theory since the ratio of their intensities depends exclusively on the ratios of the squares of the matrix elements involved.

An attempt was made using the C_{4v} basis to calculate the strength of the ^6I_J crystal-field multiplet spectra line by line. The results were inconclusive because of the approximations that had to be made. In the absence of polarized absorption data and due to uncertainty concerning the site origin of some transitions observed in the ^6I spectra, it was not possible to fit the additional parameters [the A_k^q for odd q and $\Xi(k, \lambda)$]. For the ^6P multiplets the calculation is simplified by the dominance

TABLE IV. Calculated line strengths and experimental data. The parameters used are $T_2 = 3.4 \pm 0.1 \times 10^{-10}$, $T_4 = 1.05 \pm 1.05 \times 10^{-10}$, and $T_6 = 12.2 \pm 0.05 \times 10^{-10}$. The fit is insensitive to T_4 and a value equal to half of the uncertainty is given. The calculation employed $T_4 = 0$.

Crystal-field multiplet	Oscillator strength (× 10^8) Calc	Expt
$^6P_{7/2}$	6.58	6.68
$^6P_{5/2}$	3.70	3.60
$^6I_{7/2}$	3.16	3.03
$^6I_{9/2,\ 17/2}$	24.6	24.12
$^6I_{11/2,\ 15/2,\ 13/2}$	53.6	56.82
$^6D_{9/2}$	1.54	1.11
$^6D_{7/2}$	1.83	1.92
Average deviation	0.17	

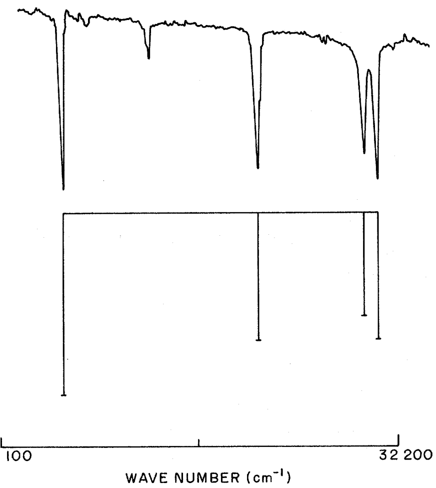

FIG. 4. $^6P_{7/2}$ crystal-field multiplet of Gd^{3+} in SrF_2 at a C_{4v} symmetry site. The calculated values are shown as vertical bars whose length is proportional to the relative strength. The 77 °K absorption spectrum shown at the top is of a sample with 0.1 mole percent nominal doping. The crystal-field quantum numbers, according to Ref. 11, are $\frac{3}{2}$, $\frac{1}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ in order of increasing wave number.

of the $U^{(2)}$ matrix elements and, consequently, the requirement for only one parameter containing $|A_0^3|^2$ and $\Xi^2(3,2)$. Since the parameters contain only terms with $q=0$, the relative strengths may be readily calculated. The comparison with experiment is shown in Fig. 4.

It might be stressed that the vectors were obtained by O'Hare (Ref. 11) from a diagonalization of the 15 lowest states of f^7 using the complete intermediate-coupling basis of Ref. 9 as zero-order wave functions. Hence, crystal-field interactions between the 15 lowest free-ion states are included to all orders of perturbation. The crystal-field states contain 33 and 34 terms of the form $|\alpha L S J J_z\rangle$ for the $\mu=\frac{1}{2}$ and $\frac{3}{2}$ representations, respectively.

There is some difficulty in assessing the quality of the fit of the three parameters T_2, T_4, and T_6. The $^6P_{7/2}$ and $^6P_{5/2}$ transitions are predominately magnetic dipole and therefore the determination of T_2 from these data is not particularly good. The calculation is insensitive to the T_4 parameter using the data available here. The T_6 parameter is determined with the greatest reliability. In spite of these difficulties the parameters were of reasonable magnitude and the fit to the experimental data is quite good.

This study neglects the high-lying sextets observed by Crosswhite *et al.*[18] in $CaF_2:Gd^{3+}$. At the present time we have not observed the characteristic site spectra in that region needed for a suitable analysis.

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