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LIE ' !RY AND DOCUMENTS SECTION

ENERGY-LEVEL ANALYSIS OF Pm^{3+} : LaC1₃

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January 1976

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LBL-4906

Energy-level analysis of $Pm³⁺: LaCl₃⁵$

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A diagonalization of the matrices representing the combined atomic and crystal-field interactions for the $4f^4$ -configuration has provided the basis for interpreting the spectrum of $Pm³⁺: LaCl₃$. Experimental data were drawn from the literature and were augmented by unpublished absorption and fluorescence results. A method of truncating the large matrices involved *is* discussed and shown to yield results in excellent agreement with complete calculations. Use of fluorescence branching ratio calculations based on the Judd-Ofelt intensity theory to monitor the interpretation of fluorescence spectra is discussed;

INTRODUCTION

In their investigation of the absorption spectrum of Pm^{3+} :LaCl₃, Baer, Conway and Davis (BCD)¹ reported extensive new experimental measurements. They deduced crystal field parameters based on splittings of four low groups but were not able to determine the atomic parameters sufficiently well to extend the analysis to states above 15,000 cm^{-1} . Previously published values derived from Pm³⁺ solution absorption spectra^{2,3,4} were similarly inadequate. To this body of experimental data we have added unpublished fluorescence and absorption measurements made at Lawrence Berkeley Laboratory. In this communication we show that an expanded parametrization of the atomic Hamiltonian provides the basis for obtaining results consistent with all available data on Pm^{3+} spectra.

In a recent paper 5 on the analysis of $\mathtt{Nd}^{\mathtt{3+}}$:LaCl₃ it was found that all observed energy levels may be accounted for to within a mean error of less than 10 cm^{-1} if effective Hamiltonian operators are included which correct for two-body and three-body electrostatic⁷ and two-body magnetic⁸ configuration-mixing effects; and also providing that the atomic and crystal-field parts of the Hamiltonian are diagonalized simultaneously. The simultaneous diagonalization insures that the sometimes considerable shifts of magnetic sub-states belonging to different atomic terms are properly taken into account. The analysis reported here for \texttt{Pm}^{3+} :LaCl₃ used the same Hamiltonian as was used for $\texttt{Nd}^\texttt{3+}$:LaCl $_\texttt{3}$; however, constraints were placed on certain poorly-defined parameters in order to make the results more consistent with other ions of the period $\left[\text{Pr}^{\mathfrak{3+}}\right]$

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 $(4f^2)$, $\frac{9}{10}$ Nd³⁺($4f^3$), $\frac{5}{5}$ Sm³⁺($4f^5$), $\frac{10}{10}$ Ho³⁺($4f^{10}$), $\frac{11}{10}$ and Er³⁺($4f^{11}$), $\frac{12}{10}$ all in the $Lac1$, host].

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HAMILTONIAN STRUCTURE

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The most extensive previous atomic parameter analysis of Pm $^{3+}$, by Carnall, Fields and Rajnak (CFR), 4 made use of intensity correlations including the identification of hypersensitive transitions in solution spectra as a basis for spectroscopic term assignments. Below 15,000 cm^{-1} there is good agreement between the conclusions of BCD and CFR, and between 15,000 and 19,000 cm^{-1} discrepancies can be resolved in favor of one or the other by calling on the greater detail of the single-crystal spectra (BCD) or the correlation of hypersensitive transitions in solution spectra with theoretical predictions (CFR). Above this point the principle difficulty in both appears to lie in approximations made in the theoretical model: (1) inadequate sets of atomic parameters were used, and (2) no account was taken of crystal-induced shifts between different atomic levels (J-mixing) .

In principle, f^4 configurations require additional, higherorder effective operators for configuration-mixing effects beyond those used for f^3 . Fortunately, the additional operators do not appear to be needed at the present level of approximation. Only the six operators which are associated with second-order perturba tion theory⁷ were used. The remaining eight which occur in higherorder theory 13 were ignored. Some correction is also needed to accomodate the variation of the spin-orbit parameter with the

spectroscopic term, but again only the part of the general set of operators which arises from second-order perturbation theory (the parameters, P^{k}) was used. 8 Spin-spin and spin-other-orbit effects are significant but were accounted for by a slightlyscaled-down Hartree-Fock calculation. Their inclusion did not, therefore, increase the number of variable parameters in the initial diagonalizations.

The crystal-field interactions themselves were treated by conventional theory which uses only single-particle operators. There is a fairly clear indication in the \Pr^{3+} and \mathtt{Nd}^{3+} cases that higher-order corrections are needed. However, they appear to involve energy level shifts of less than 15 cm^{-1} , which is the level of residual error which we have found for all lanthanide cases studied in this detail. $5, 9, 10, 11$

Comparison of the Nd^{3+} , Ho³⁺, and Er^{3+} results cited previously indicated that the configuration-mixing corrections are nearly constant across the series. We could consequently begin the Pm^{3+} analysis by fixing these corrections at the Nd^{3+} values. In addition, it has been found that the Slater parameters, F^{K} , as well as the spin-orbit parameter, ζ , can be related to a priori calculations by a nearly constant correction. 14 Our initial interpretation of the energy level scheme of Pm^{3+} was therefore based on good estimates of the magnitudes of all of the important interactions.

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0 0 0 0 4 5 0 3 1 9 7

DIAGONALIZATION METHODS

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In the $Nd^{3+}(4f^3)$ case for a relatively high (C_{3h}) symmetry in the neighborhood of the rare earth ion, the Hamiltonian may be separated into three submatrices, the largest of which is of rank 62. This is of a size which is conveniently handled by modern computers and for that case least-squares parameter calculations of the Hamiltonian could be obtained without approximation. In the present case, as for $ho^{3+}(4f^{10})$, the matrices are somewhat larger (ranks up to 171), which although not too large in principle, in practice·are cumbersome. We therefore devised an approximation method which is more than adequate for the $4f⁴$ problem and which also has proven useful for the larger matrices of the middle-period ions. We carry out the following series of operations:

(1) The field-independent part of the Hamiltonian is diagonalized separately for each appropriate J-value using estimated parameters. Reduced matrix elements (SLJ $||c^{(k)}||$ SL'J') are computed and stored for appropriate values of the crystal field operator rank (2, 4, or 6).

(2) The eigenvectors derived from this diagonalization are then used to transform all Hamiltonian matrices (including the reduced $C^{(k)}$ ones) to this new intermediate-coupling basis. At this point we now reject all states above a certain selected energy which was 35,000 cm^{-1} for the present case. In general we have found it convenient to limit the truncated matrix to about rank

80. Comparison with diagonalizations in which the full matrices were used showed errors of 2 cm^{-1} or less, which is small enough compared to the residual errors that for intermediate investigations they were quite adequate, at about one quarter the computer time requirements. In the present case, the complete matrices were used for the final calculations.

EXPERIMENTAL

Energy levels derived from absorption spectra were from $BCD¹$ except for one set of data not previously reported which was taken in the ultraviolet range using a 0.1% \texttt{Pm}^{3+} :LaCl₃ crystal at liquid nitrogen temperature. The fluorescence spectra reported here were obtained at 25°C in two different experiments using different crystals. The doping in each case was of the order of 0.18 Pm^{3+} : $Lac1$,.

REASSIGNMENT OF QUANTUM NUMBERS --~----------------------------

In the course of a recent study of the spectra of Np^{3+} in LaCl₃ and LaBr₃, ¹⁵ it was pointed out that all available data indicate an identical crystal-field quantum number ordering for equivalent pairs of trivalent actinide and lanthanide ions in LaCl₃. Since the ordering reported in Np^{3+} and Pm^{3+} (both f^4 species) differed, and the assignments for $\texttt{Np}^\texttt{3+}$ were based on more extensive experimental results, 16 a re-examination of the interpretation of the pm^{3+} :LaCl₃ data was suggested. The results of the new analysis are shown in Table I which also gives all basis states that contributed >0.1% to the eigenvectors. The assignments are compared below:

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The energy of even the highest component of the ground state could be established from the absorption measurements reported by BCD, but the interpretation of the fluorescence spectrum of Pm^{3+} : LaCl₃ for those transitions terminating in the ground state, as shown in Table II, was also fully consistent with the present analysis. The energies and assignments in Table I together with the electric dipole selection rules for the $C_{3h}^-(D_{3h})$ symmetry, provided the basis for an essentially complete analysis of the absorption data of BCD as shown in Table III. A few weak levels could not be interpreted. Several impurity lines were identified. In the latter case, the energies and polarization were consistent with very strong lines previously identified in the spectra of the impurity in LaCl₃.¹⁷ A number of strong lines at >27,000 cm⁻¹ could not be \sqrt{c} assified using the present interpretation of the Pm3+ spectrum.

In agreement with BCD, we found that it was difficult to develop a consistent analysis solely on the basis of previously existing experimental data .

As was noted earlier, there *is* good agreement between the assignments of free-ion states made by BCD and those made earlier on the basis of intensity correlations in the spectrum of Pm³⁺ (aquo) at energies <15,000 cm^{-1} . It is now apparent that several incorrect assignments were made to the solution spectrum at >15,000 cm^{-1} beginning with the assignment of both the ${{}^5\text{F}}_5$ and ${{}^3\text{K}}_6$ states to a weak band near 16,000 cm^{-1} . The results of BCD provide clear evidence that only the ${}^{5}F_{5}$ state occurs at this energy. However, the solution spectrum also provided the insight for-reassigning some of the levels in the crystal. For example, the two strong lines at 17512.6 and 17537.5 cm^{-1} in Pm $^{3+}$:LaCl₃ correlate well with the structure expected for the $56₂$ state which had previously been assigned near this energy based on arguments which identify it with hypersensitive transitions found in solution. 4 , 18 In addition, the intensity calculations identified strong somewhat isolated absorption bands observed in solution near 30,000 cm^{-1} with transitions to the 5 D_{0,1,2} states.^{4,19} Previously unpublished absorption spectra of Pm^{3+} :LaCl₃ taken at liquid nitrogen temperature in the range $28,000-32,000$ cm⁻¹ (Table III) exhibit features that are consistent with the solution spectrum. There is a constant \sim 400 cm⁻¹ shift between the groups of levels identified in the crystal as belonging to the ${}^{5}D_{0,1,2}$ states and those assigned *in* solution.

Most of the transitions observed in fluorescence could be interpreted as having their origin *in* levels that had also been . observed in absorption. In addition, transitions to the 5 I₅,6,7,8 groups were identified. The energies associated with

 0.00004503199

the latter two groups in Pm^{3+} :LaCl₃ were essentially the same as those observed in absorption in solution. 18 The results reported in Table II include all the line groups previously cited as characteristic of the luminescence spectrum of PmCl₂.²⁰

Figure 1 shows a schematic energy level diagram for Pm^{3+} :LaCl, including all classified fluorescence transitions, according to the detailed account given in Table II.

CRYSTAL-FIELD ANALYSIS -~--------------------

The details of the complete diagonalization procedure were discussed earlier and are also given in reference 5. In the present case, a preliminary crystal-field calculation using approximate parameters correlated well with most of the observed crystal field level energies. Assignments were then made and a number of diagonalizations carried out in which increasing numbers of parameters were freely varied. Several additional assignments were made based on correlations between calculated and observed energies and correct polarization. In the final diagonalization, most of the atomic and all of the crystal field parameters were freely varied. The results are given in Table IV.

The crystal-field parameters established here were in relatively good agreement with those determined by BCD. It is now apparent that the parameters they reported actually give the same crystal-field quantum number ordering of the ground state as was deduced for Np^{3+} :LaBr₃, ¹⁶ not the ordering reported in reference 1.

For purposes of comparison with free-ion level calculations and the identification of free-ion states, the results shown in Table V were calculated with the atomic parameters of Table IV but with the crystal-field parameters set equal to zero. These levels represent the unperturbed centers of the crystal groups. Deviations from the numerical centers of the computed Stark components are a measure of the so-called J-mixing shifts. (In making this average, one must remember to give the doubly-degenerate $\nu = 1$ and 2 levels double weight.)

FLUORESCENCE LIFE-TIME CALCULATIONS AND THE INTERPRETATION OF --~------------------ FLUORESCENCE DATA

Recently, Krupke²¹ calculated the radiative transition probabilities from the $^{5}F_{2}$ and $^{5}F_{1}$ states (~12,500 cm⁻¹) in Pm³⁺:YAG, and pointed out that such a system would in principal make an excellent 0.92μ laser. The theory used in making that prediction is of interest to the present investigation. In the absence of selective excitation results, the assignment of the room temperature fluorescence data (Table II) was based on fitting energy differences that were consistent with the calculated energy level scheme and with the applicable selection rules. It is of interest to determine whether the assignments are also consistent with the branching ratios that can be calculated for transitions arising from a given fluorescing level.

The calculation of the life-times of fluorescing levels in rare earth doped crystals using the Judd-Ofelt intensity theory^{22,23}

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has been discussed in detail in several publications.^{24,25} The spontaneous electric dipole emission probability of an excited state (ψ J) with respect to a particular lower-lying state (ψ' J') can be written:

$$
A(\psi J, \psi' J') = \frac{64 \pi^4 e^2}{3h} \frac{\sigma^3}{(2J+1)} \frac{n (n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_{\lambda} (\psi J ||U^{(\lambda)}|| \psi' J')^2
$$

where σ is the energy difference between the states, n is the refractive index of the host crystal, the Ω_{χ} 26 are Judd-Ofelt parameters evaluated from absorption spectra data, and the $U^{(\lambda)}$ are unit tensor operators connecting the initial and final states.

The total spontaneous electric dipole emission rate from an initial state is the sum over the rates to each of the free-ion states into which decay can occur,

$$
A_{T}(\psi J) = \sum_{i} A(\psi J, \psi' J')
$$

The radiative lifetime of the initial state is then $\tau = [A_{\tau}(\psi J)]^{-1}$ and the branching ratio, R_i' , to any given final state is $R_i =$ $A(\psi J,\psi^*J^*)$ $[A_{\tau}(\psi J)]^{-1}$. In addition to the radiative mode, an excited state may relax by multiphonon emission.²⁷ In the present case, interest centers for the most part on levels where spontaneous emission is the primary relaxation process.

Selected results of the branching ratio calculations from levels assigned in Table II as the principal fluorescing states are given in Table VI. In addition to identifying the final states consistent with the largest branching ratios, the computed radiative lifetimes of the initial states are given. The correlation between average group intensities and predicted branching ratios

is of course expected to be only approximate. Nevertheless, much of the data in Table II appears to be consistent with the predicted trends. There is a greater average intensity associated with larger branching ratios. In some instances the interpretation was strongly influenced by the calculations. For example, the original assignment of lines extending from-17256.5 to 17478.3 cm⁻¹ to the transition $Q + V$ was consistent in energy and polarization, but there are no $U^{(\lambda)}$ matrix elements connecting these states. An acceptible alternative. was found.

Comparison of the data given in Table VII for $Pm³⁺: LaCl₃$ with that for Pm^{3+} :YAG, 21 illustrates the much longer radiative life-times associated with the LaCl₃ host. While the matrix elements of $U^{(\lambda)}$ computed here in intermediate coupling are -·· somewhat different from those used in reference 21, the smaller n_A parameter values are clearly the main source of the different life-times. We assume that values determined for $\mathtt{Nd}^{\mathtt{3+}}$:LaCl $\mathtt{j}^{\mathtt{28}}$ are a reasonable approximation of those for Pm^{3+} :LaCl₃. As in Pm^{3+} :YAG, the ${}^{5}F_1$ + ${}^{5}I_5$ transition remains the principal channel for radiative relaxation of the ${}^{5}F_{1}$ state, so Pm³⁺:LaCl₃ should also provide coherent laser action at $\sqrt{0.92}$ μ at room temperature.

Branching ratio calculations based on the Judd-Ofelt theory appear to be a potentially useful supportive basis for the interpretation of fluorescence spectra of f-electron systems. This is the complement of the use of intensity relationships observed in absorption spectra as one basis for making energy level assignments.4

Table I. Ground State of $Pm:LaCl_{3}({}^{5}I_{4})$

a
The parameters used to compute these values are given in Table IV.
DComponents comprising >0.1% of the eigenvectors are included.

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Wavenumber	I^a	Lower ^b	$\texttt{Upper}^{\texttt{b}}$	$O - \Delta E^C$
(cm^{-1})		Level	Level	
12084.2	$\langle 8 \rangle$	$Z_6(3)$	$A_1(1)$	-9
099.5	10	2^{6}	$A_2(0)$	-10
222.5	7	$2_{4}(2)$	A_1	-11
237.3	10	\mathbf{z}_4	A_{2}	-12
258.4	10	$\frac{z_3(3)}{2}$	A_{2}	-6
319.8	9	z_{1}	A_1	-14
338.2	8	\mathbf{z}_{1}	A_2	-11
12516.4	6	$\frac{z}{6}$ (3)	$B_1(1)$	$\mathbf{1}$
645.8	3	$2_{5}(0)$	$B_2(2)$	\cdot 2
663.9	6	$2_{4}(2)$	B_{2}	-7
682.0	$\overline{\mathbf{c}}$	$\frac{z}{3}$ (3)	B_2	-4
706.2	5	\mathbf{z}_4	$B_3(0)$	-5
721.5	5	\mathbf{z}_3	B_3	-5
751.9	5	$Z_1(2)$	B_1	-6
782.6	ı	\mathbf{z}_1	B_{2}	-12
807.1	$\mathbf{2}$	z_1	B_3	-4
13577.7	$\overline{\mathbf{3}}$	$Z_1(2)$	$C_2(2)$	-11
602.3	$\mathbf{3}$	z_1	$C_3(0)$	-4

TABLE II. Fluorescence Spectrum of Pm^{3+} :LaCl₃ at 25°C.

TABLE II (Continued)

TABLE II (Continued)

0 0 0 0 4 5 0 3 2 0 1

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TABLE II (Continued)

TABLE II (Continued)

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 a Relative intensity.

 b The p -values associated with the indicated levels are shown in parentheses. For definition of the letter symbols and for their numerical correspondence, see Table III.

 ${}^{\text{c}}$ Difference between the energy of the transition observed in fluorescence (col. 1) and that deduced from the levels observed in absorption (col. 4-co1. 3).

TABLE III. Energy levels and absorption spectra of Pm^{3+} :LaCl₃.^a

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TABLE III (Continued)

 458.4 1

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TABLE III (Continued)

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TABLE III (Continued)

 $5s₂$

 5_{f_4}

 $5F_5$

 $23[°]$

TABLE III (Continued)

 $5F_{5}$

 $\frac{3}{k_6}$

 900.0 $\mathbf{1}$ $\overline{2}$ -1.3 F_{4} z_1 908.8 $6 \overline{6}$ 910.0 $\mathbf{1}^{\mathbf{1}}$ -4.2 F_5 z_1 \overline{c} 912.8 \mathbf{I} 2.3 F_6 $\overline{\mathbf{3}}$ 919.9 (15921.9) $\overline{3}$ Z_3 G_3 16809.8 $\mathbf{1}$ 820.8 \overline{z}_4 G_{5} T $z₂$ G_3 827.3 \mathbf{I} 836.4 (2) G_{5} $2₃$ $\mathbf{1}$ 836.4 $\mathbf{2}$ z_{2} $G_{\tilde{A}}$ (1) -9.0 z_1 \overline{c} G_{1} 883.0 $\mathbf{3}$ $\overline{\mathbf{0}}$ -12.4 z_{1} $G₂$ 887.5 $\ddot{\mathbf{4}}$ -7.7 G_3 z_1 \mathbf{I} 893.8 5 4 (15928.7) $\overline{\mathbf{3}}$ $-2.3, -13.7$ $0,2$ z_1 G_{4} 903.1 4 (16909.6) $\overline{\mathbf{3}}$ 7.2 $\mathbf{1}$ 920.6 z_1 G_5 4 14.6 z_{1} G_{6} $\bf{0}$ 926.9 \mathbf{I} Z_5 H_2^- 17388.1 J. Z_{4} $H₂$ 415.5 $\overline{2}$ $6\overline{6}$ H_1^{\parallel} (Z_3 428.0 6 \overline{z}_4 5 H_3 437.8

 $24[°]$

0 0 0 $\mathbf{5}$

TABLE III (Continued)

TABLE III (Continued)

 $\frac{3}{5}$ K₈

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TABLE III (Continued)

 5_{G_5}

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 363

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 ${}^{3}G_{3}$ 674.0 4 ${}^{2}1$ M₂ 0 -0.2 363 680.0 8 2 Z_1 M₃ 2,3 -17.3,2.6 691.0 3 9 M₄ 3 (21719.8) 727.5 3 $^5\!{\rm G}_5$ 22081.3 2 Z_2 N₄ 106.9 8 Z_1 N₁ 1 -4.8 0 (22115.2) 127.9 6 Z_1 N₂ 2 -4.6 140.5 6 Z_1 N₃ 1 -2.3 3 (22144.1) 149.3 4 Z_1 N₄ 2 -3.9 3 {22177.0) 566 ⁶226.2 2 247.5 2

TABLE III (Continued)

3 (22262.8) 2 (22298.8) 3 (22326.4) 0 (22353.5) 2 (22357.6) 1 (22357.9) 0 (22360.8) 396.0 2 Z_1 N_5 1 -2.7 0 (22404. 1)

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 \overline{O} 7 \mathbf{z} O

 $29²$

TABLE III (Continued)

31

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TABLE III (Continued)

TABLE III (Continued)

 3_{P_1} , 3_{D_1}

 $3p₂$

 3_{I_5}

 $36₅$

 (27848.3) $\mathbf 0$ (28613.5) $\mathbf 0$ 28632.8^e $2(2)$ $AA₁$ $\overline{2}$ $\overline{3}$ (28656.7) 1 (28749.1) $\bf{0}$ (28754.2) $\mathbf{1}^{\text{max}}$ 758.0 $\overline{\mathbf{3}}$

 $\mathcal{P}_{\mathcal{A}}^{\mathbf{v}}=\mathcal{P}_{\mathcal{A}}^{\mathcal{A}}$

33

 (27152.6)

 (27188.9)

 (27836.1)

 -2.6

 $\label{eq:3.1} \mathcal{O}^{(2\pi)}\left(\mathcal{V}^2_{\mathbf{F}}\right)^{-\frac{1}{2}}=\mathcal{O}(\sqrt{1-\epsilon})$

 $\overline{3}$

 \overline{c}

 $\begin{array}{c} \rule{0pt}{2ex} \rule{0pt}{$

TABLE III (Continued)

10 000045032

TABLE III (Continued)

 $3\begin{array}{c} 3 \end{array}$

 3_{M10}

 $\overline{}^5$

 $3_{N₁₀}$

 $5D_{1}$

 3_M ₁₀

 30034.0^e

 $3w$

 z_j

 (30110.3)

 (30141.2)

 (30192.3)

 \overline{c}

 $\mathbf{0}$

 $\mathbf 0$

 $DD₁$

TABLE III (Continued)

 $3_{M_{10}}$

 3_{I_7}

 $1_{L_{8}}$

 5_{D_2}

 (30200.2) (20208.0) (30210.5) (30381.5) (30400.4) (30409.1) (30424.8) (30425.8) (30428.9) (30445.7) (30448.7) (30449.4) (30456.9)

 36

 $\overline{\mathbf{3}}$

 \overline{c}

 \mathbf{I}

 \mathbf{I}

 $\mathbf 0$

 $\mathbf{1}$

 $\pmb{0}$

 $\mathbf 0$

 $\mathbf{2}$

 $\overline{\mathbf{3}}$

 $\mathbf{1}$

 $\overline{3}$

 \overline{c}

TABLE III (Continued)

 5_{0}

 $_{\sf b}^{\sf d}$ Data from Ref. 1 except as noted.

bThe difference between the observed and calculated levels, the latter based on the parameters recorded in Table IV, is given. When no corresponding level _cwas observed, the calculated level is shown in parentheses.
_dLevel obtained from fluorescence data.

Level obtained in absorption from higher levels.

Unpublished absorption at 77°C, unpolarized.

TABLE IV. Parameters for Pm^{3+} :LaCl₃ energy levels.

TABLE IV (Continued)

^aThis parameter value was based on analyses of other lanthanide chloride spectra and was not varied.

 b Only M⁰ was freely varied, M² and M⁴ were constrained to vary in the ratios $M^2/M^0 = 0.56$ and $M^4/M^0 = 0.38$.

 $^{\text{c}}$ Only P² was freely varied, P⁴ and P⁶ were constrained to vary in the ratios $P^4/P^2 = 0.75$ and $P^6/P^2 = 0.5$.

.796³ $K2 - .441$ ³ $K1$

 $.756³$ K2 - $.386³$ K1

 $-.698⁵$ G-.428³H4

 $.810^5$ G-.399⁴H4

 $.676^5$ G-.498³H4

 $.912^5$ G+.315³H4

 $-.724$ ³G2+.470³G3

18214

19803

20006

20155

21694

22145

22343

 $\overline{\mathbf{K}}$

L

 ${\bf M}$

N

 $\overline{7}$

8

 $\overline{5}$

 $\overline{\mathbf{4}}$

 $\overline{3}$

5

 $\overline{6}$

Field-free levels of Pm^{3+} :LaCl₃ TABLE V.

1.0008

1.0978

1.1818

1.0340

0.7871

1.1415

1.3052

 $\ddot{\mathcal{S}}$ \ddot{Q} \bullet $\mathcal{L}% _{0}\left(t\right) \equiv\mathcal{L}_{\mathcal{A}}\left(t\right) .$ **BORNER** نې
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TABLE V (Continued)

^aFrom Table III.

 $^{\text{b}}$ All calculated states <32,000 cm⁻¹ are recorded. The energy given was computed using the atomic parameters shown in Table IV. Values put between parentheses are for levels for which there were no experimental observations.

 0 0 0 0 4 5 0 3 2 \mathcal{L}

TABLE VI. Fluorescent branching ratios and lifetimes from selected states (SLJ) in Pm^{3+} :LaCl₃.^a

Group Symbol ^b	SLJ	σ $(cm^{-1})^C$	$\overline{\tau_R^d}$ usec	$\mathbf{5}_{\mathbf{I}_{4}}$	Branching ratio to S'L'J' 5_{I_5}	$^{5}I_{6}$	5_{I_7}	$\mathbf{^{5}I}_{8}$	
A	$5F_1$	12332	625	.28	.43	.26	.03	0	
B	$5F_2$	12774	585	.42	.31	.16	.09	.01	
$\mathbf c$	$5F_3$	13621	510	.52	.18.	.13	.13	.04	
$\mathsf F$	$5F_5$	15903	525	.04	.12	.27 ₂	.34	.23	
$\mathbf G$	$3_{K_{6}}$	16916	14030	.36 [°]	.49	.03	.09	.03	
H°	5_{G_2}	17535	176	.68	.24	.06	.01	$10E - 3$	
$\mathbf{\hat{K}}$	$\frac{3}{5}$ K ₈	19803	7068	.14	.05	.12 ₁	.43	.22	
M	3_{G_3}	21694	670	, 24	.54	.41 ₁	.05 ₀	.01	
$\overline{\mathsf{N}}$	$56\overline{6}$	22145	305	.06	.12	.28	.37	.09	
N'	566	22343	181	.002	.02	.10 ₁	.26	$.53 -$	
$\pmb{0}$	$\frac{3}{2}D_2$	22944	1192^-	.10	.42	.38	.002	$10E - 3$	
Q	3_{D_1}	24022	1611	.01 [°]	.60	.12	.04	$\mathbf 0$	
U	σ_{F_4}	27020	565	.007	.02 ₁	.03	.11	.35	

^aThe intensity parameters used in the calculation were $\Omega_2 = 0.97$, $\Omega_4 =$ 1.63, $\Omega_6 = 1.66$ (all x 10⁻²⁰ cm).²⁸

bGroup symbol of fluorescing state from Table III.

^CThe energy of the fluorescing state with respect to the ground state

 ${}^{5}I_{4}$ calculated from the parameters in Table IV is given.

d_{Total} radiative lifetime of the fluorescing state.

TABLE VII. Calculated transition probabilities^a and matrix elements^b of $U^{(\lambda)}$ from the 5F_1 state in Pm^{3+} :LaCl₃.

$(\psi J)^{-}$	$(\psi'J')$ σ -1 cm	$\left[\frac{1}{2}\right]^{2}$ $\left[\frac{1}{2}\right]^{2}$		A \mathcal{L} S.	τ_{ψ} ្វេរ ms	τ rad μ sec
$5F$.	12228	0.1406	0.0	456.5	2.19	
	$5_{I_{5}}$ 10739	0.1533	0.1545	683.2	1.46	
	$^{5}I_{6}$ 9116	0.0	0.2989	409.5	2.44	625
	5 I, 7408	0.0	0.0680	49.99	20 _o	
	5. 5648 ⊥8	0.0	0.0	0	∞	$\frac{1}{2}$ and $\frac{1}{2}$

^a Based on intensity parameters for Nd^{3+} :LaCl₃, given in Table VI.

 b The matrix elements of $y^{(2)}$ for the indicated transitions are

zero.

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FIGURE CAPTION

Figure 1. Schematic energy level diagram for Pm^{3+} :LaCl₃

including all classified fluorescence transitions.

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