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Configuration Interaction and the Spectra of $LaCl_3:Pr^{3+}$ [†]

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Effective operators, which take into account the excitation of a $4f$ electron to a higher-lying p or f orbital by means of the crystal field, are cast into a form which is convenient for a parametric study. The complete crystal-field matrices of these operators and of the operators that arise in the first-order analysis are diagonalized, and the Stark levels of $LaCl_3:Pr^{3+}$ are fitted parametrically. It is found that when the effect of configuration interaction is absorbed by these new parameters, the ordinary crystal-field parameters change by a small but significant amount.

I. INTRODUCTION

Analysis of the optical spectra of rare-earth ions in crystals has thus far depended upon the "free-ion" model. According to this approximation, the free-ion parameters are evaluated by fitting the centers of gravity of the Stark multiplets. The crystal-field parameters are then obtained either by perturbation theory[1] or by computing the complete crystal-field matrices.[2] One difficulty with this approach is that the crystal field induces mixing between different "free-ion" levels and shifts their mean position. Although these shifts have been estimated in some cases,[2,3] they nonetheless introduce an imprecision into the analysis, which can entirely mask small effects such as the two-body magnetic interactions.[4] Another difficulty with this approach is that since the free-ion parameters and the crystal-field parameters are not allowed to vary simultaneously, the screening of the crystal field by the electrons is not fully taken into account. Values of the crystal-field parameters, which are obtained in this way, tend to be too small.

Another feature of most of the treatments of rare-earth ions in crystals is the assumption that the ground electronic configurations are pure $4f^N 5s^2 5p^6$ and that the spectra arise from transitions within these configurations. While several authors[1,2,5] have recognized the limitations of such an approximation, few attempts have been made to take into account the perturbing effects of higher-lying configurations. Wong[6] has found that by considering the interaction of $4f^2$ with $5d^2$ the fit of the centers of gravity of the spectra could be improved. Rajnak[3] has explicitly calculated the perturbing effects of the $4f\,5f$ and $4f\,6p$ configurations upon the Stark structure of $4f^2$. She was not able to obtain, however, an improvement of the fit for $PrCl_3$, and concluded that the perturbing effects of other configurations are important. More recently, Rajnak and Wybourne,[7,8] Wybourne,[9] and Armstrong[10] have introduced effective operators which take into account the perturbing effects of all higher-lying configurations to second order in perturbation theory.

The purpose of this paper is to consider the effect of operators of this kind upon the Stark structure of $LaCl_3:Pr^{3+}$. The effective operators, which take into account the excitation of a $4f$ electron to a higher-lying p or f orbital by means of the crystal field, are cast into a form which is convenient for a parametric study. The complete crystal-field matrices of these operators and of the operators that arise in the first-order analysis are diagonalized and the Stark levels of $LaCl_3:Pr^{3+}$ are fit parametrically. A considerable improvement in the fit is obtained.

II. FIRST-ORDER THEORY

The crystal-field potential at an ion site of C_{3h} symmetry may be described by adding to the free-ion Hamiltonian an effective operator of the form

$$H = A_0^2 U_0^{(2)} + A_0^4 U_0^{(4)} + A_0^6 U_0^{(6)} + A_6^6 (U_6^{(6)} + U_{-6}^{(6)}) + B_6^6 (U_6^{(6)} - U_{-6}^{(6)}).$$

The tensor operators $U^{(k)}$ have been tabulated by Nielson and Koster.[11] Since the Pr^{3+} site has an approximate D_{3h} symmetry, we expect the parameter B_6^6 to be small. The $|JM\rangle$ basis functions for the four irreducible representations of the C_{3h} group are listed in Table I. The states $|J, -2\rangle$, $|J, 4\rangle$, $|J, -1\rangle$, and $|J, +5\rangle$ have been omitted since they are related by time reversal to states which do appear in the table, and hence lead to degeneracies.

The four crystal-field matrices of H_{cf} and of the free-ion Hamiltonian were diagonalized and fitted to the Stark levels reported by Sayre *et al.*,[12] and by Dieke and Sarup.[13] The results are shown in the first column of Table II. The parameters P_k which correspond to the electrostatically correlated spin-orbit interaction,[4] were poorly determined, and an additional fit was performed in which these

TABLE I. Basis functions for the irreducible representations of C_{3h}.

Γ_1	$\lvert J, 0\rangle$,	$\lvert J, 6\rangle$,	$\lvert J, -6\rangle$
Γ_2	$\lvert J, 3\rangle$,	$\lvert J, -3\rangle$	
Γ_3	$\lvert J, 2\rangle$,	$\lvert J, -4\rangle$	
Γ_4	$\lvert J, 1\rangle$,	$\lvert J, -5\rangle$	

parameters were held at zero. In this second fit a single parameter η was introduced which allows for the expansion of the $4f$ wave function as the energy is increased.[14]

The crystal-field parameters which we have obtained and those obtained previously by Margolis[2] are given in the first two rows of Table III (in our normalization). Margolis's values are smaller than ours. As we mentioned above, this is due to the way Margolis carried out the fitting procedure. He obtained a set of free-ion parameters by fitting the centers of gravity of the Stark multiplets. He then held the free-ion parameters constant and adjusted the crystal-field parameters to fit the individual Stark components. When, instead, all of the parameters are allowed to vary simultaneously (as they have in our fit), the free-ion parameters adjust in such a way as to minimize the effect of the crystal field, and larger crystal-field parameters are required to produce the observed splitting. We have performed a number of fits with the free-ion parameters fixed and have confirmed this general behavior. Margolis's procedure, which has come to be called the "free-ion theory," does not fully take into account the screening of the crystal field by the electrons.

One feature which is common to our analysis and to that of Margolis is the relatively poor agreement obtained for the $^1D_2$ multiplet (Fig. 1). Although the rms deviation for all of the levels is 6.6, the difference between observed and calculated values for this multiplet are 22.0, -15.8, and -6.4. Since we have formed the complete crystal-field matrices within f^2, effects of this kind must be due to configuration interaction.

III. CONFIGURATION INTERACTION

The noncentral part C of the Coulomb interaction is the largest of the terms in the perturbative Hamiltonian, and is mainly responsible for mixing

TABLE II. Fit to crystal-field levels of $LaCl_3:Pr$. Parameters in brackets were held constant at the indicated values.

Parameter	Fit *A*	Fit *B*	Fit *C*	Fit *D*
E (*AVE*)	6688.6 ± 51	6698.9 ± 12	6709.4 ± 13	6706.8 ± 7.4
E 1	4874.6 ± 34	4872.7 ± 5.7	4864.4 ± 11	4866.6 ± 5.0
E 2	22.291± 0.34	22.252± 0.05	22.201± 0.08	22.220± 0.03
E 3	471.16 ± 7.1	469.59 ± 1.1	468.60 ± 1.7	468.96 ± 0.65
ζ	762.25 ± 9.5	757.00 ± 1.0	756.79 ± 2.5	757.34 ± 0.61
α	24.319± 1.2	23.907± 2.8	23.335± 0.5	23.394± 0.42
β	-597.97 ± 73	-610.06 ± 16	-611.71 ± 22	−607.87 ± 14
γ	[0.0]	[0.0]	[0.0]	[0.0]
$M(0)^a$	0.430± 0.94	1.710± 0.14	1.762± 0.12	1.784± 0.08
$M(2)^a$	0.241	0.957	0.987	0.999
$M(4)$	0.164	0.650	0.670	0.678
$P(2)$	- 0.410± 0.95	[0.0]	0.061± 0.28	[0.0]
$P(4)$	- 0.522± 0.38	[0.0]	[0.0]	[0.0]
$P(6)$	- 0.120± 0.20	[0.0]	[0.0]	[0.0]
$A2(0)$	-151.92 ± 10	-152.08 ± 9.9	-187.17 ± 13	-187.25 ± 13
$A4(0)$	-376.13 ± 26	-374.67 ± 25	-280.82 ± 68	-280.99 ± 66
$A6(0)$	835.81 ± 37	835.35 ± 36	867.36 ± 24	867.20 ± 23
$A6(6)$	-762.66 ±110	-767.22 ±110	-541.69 ±140	-540.09 ±140
$A6(-6)$	205.87 ±120	214.18 ±110	9.942±140	8.693±140
$R(2)$ $D2$			-214.17 ± 94	-214.19 ± 91
$R(2)$ $D4$			[-26.823]	[-26.823]
$R(2)$ $F2$			391.49 ±170	392.35 ±160
$R(2)$ $F4$			-790.00 ±440	-790.25 ±430
$R(2)$ $F6$			-252.34 ±200	-255.10 ±200
$R(4)$ $P2$			[-276.95]	[-276.95]
$R(4)$ $P4$			473.63 ±440	472.30 ±430
$R(4)$ $F2$			653.30 ±710	651.36 ±690
$R(4)$ $F4$			1357.4 ±470	1351.8 ±450
$R(4)$ $F6$			-1795.6 ±1000	-1803.9 ±1000
η	0	691.43 ±110	617.12 ±180	656.51 ± 63
error	6.5	6.6	3.1	3.1

[a] Only $M(0)$ was freely varied. The ratios $M2/M(0)$ and $M(4)/M(0)$ were held to Hartree-Fock values.

TABLE III. Comparison of empirical and calculated parameters.

	A_0^2	A_0^4	A_0^6	A_6^6
Margolis (with "free-ion" treatment of electronic parameters)	-129	-366	810	-545
Complete diagonalization, but without configuration interaction	-152	-375	835	-767
With configuration interaction	-187	-281	867	-540
Calculation of Ellis and Newman without charge penetration and covalency	-467	-397	613	-483
With charge penetration and covalency	-380	-370	736	-588

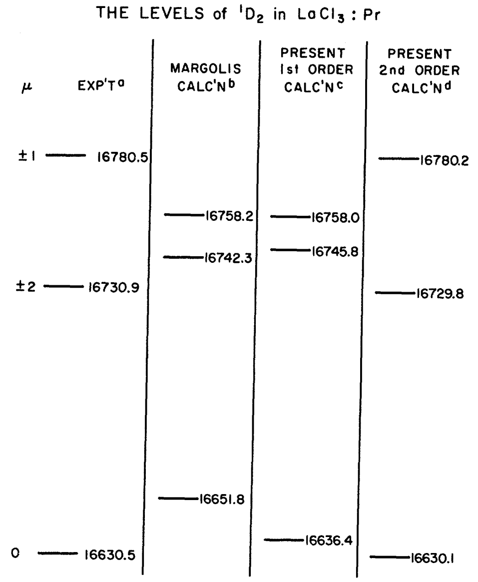

FIG. 1. Levels of $^1D_2$ in LaCl$_3$: Pr.

configurations. All matrix elements $\langle\psi|H|\psi'\rangle$ of the ground configuration should thus be corrected by terms of the type $\langle\psi|H_{\rm ci}|\psi'\rangle$, where

$$H_{\rm ci}=-\sum_\chi H_{\rm cf}|\chi\rangle\langle\chi|C/\Delta E-\sum_\chi C|\chi\rangle\langle\chi|H_{\rm cf}/\Delta E$$

and where χ runs over all the states of the perturbing configurations. Since the crystal-field interaction $H_{\rm cf}$ is a one-body operator and C conserves parity, the only configurations which contribute to this sum are those for which a single electron is excited to a state of the same parity. The effect of the one-body part of $H_{\rm ci}$ is absorbed by the crystal-field parameters.

$H_{\rm cf}$ may be written generally

$$H_{\rm cf}=\sum_{k,q}A_{kq}\sum_i r_i^k C_q^{(k)}(\theta_i,\phi_i).$$

Using graphical techniques, the two-body part of $H_{\rm ci}$, which is due to the excitation of a nl electron to a higher-lying $n'l'$ orbital, can readily be putt in the form

$$H_{\rm ci}{}^{(2)}=\sum_{l'}\sum_{k,q,k'}R_{l'k'}^{(k)}S_q^{(k)}, \tag{1}$$

where

$$\vec{S}^{(k)}=\tfrac{1}{2}\sum_{i>j}\sum_{k''}[1+(-)^{k''}](2k''+1)\times\begin{Bmatrix}k & l & l'\\ l & k' & k''\end{Bmatrix}\left\{\vec{U}_i^{(k')}\vec{U}_j^{(k'')}\right\}^{(k)} \tag{2}$$

and

$$R_{l'k'}^{(k)}=-4\sum_{n'}(2k+1)^{-1/2}(l\|C^{(k')}\|l)\times(l\|C^{(k')}\|l')(l'\|C^{(k)}\|l)R^k(ll,ll')\times(nl|r^k|n'l')A_{kq}/(E_{n'l'}-E_{nl}). \tag{3}$$

The Feynman graph, which corresponds to the effective operator $\vec{S}^{(k)}$ is given in Fig. 2(a). Although, we have considered only the excitation of a $4f$ electron to another shell, the parameters $R_{l'k'}^{(k)}$ also absorb the effect of excitations of inner electrons to the $4f$ shell[8] [Fig. 2(b)]. There are, of course, other possible second-order processes.[10] However, for Pr^{3+} the Coulomb interaction produces much larger effects than either the spin-orbit or the crystal-field interaction, and the effective operators $\vec{S}^{(k)}$ should represent the dominant effect.

For an ion at a site of D_{3h} symmetry, four operators $\vec{S}^{(k)}$ are required to absorb the effect of excitations of a $4f$ electron to a p shell and twelve are required to absorb the effects of excitations to an f shell. One way to limit the number of additional parameters is to use Rajnak's eigenfunctions,[15] for the terms $l=5f$ and $l=6p$ in the summation of Eq. (3), and in this way estimate which of the second-order operators are more important. However, since Rajnak[3] was not able to obtain a reasonable

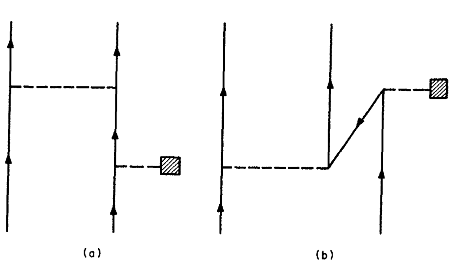

FIG. 2. Feynman diagrams used to obtain $\vec{S}^{(k)}$.

TABLE IV. Reduced matrix elements of the $\vec{S}^{(2)}$ for the configuration f^2.

ψ	ψ'	F[a]	$\vec{S}^{(2)}_{p2}$	$\vec{S}^{(2)}_{p4}$	$\vec{S}^{(2)}_{f2}$	$\vec{S}^{(2)}_{f4}$	$\vec{S}^{(2)}_{f6}$
^1S	^1D	$(42)^{1/2}/11$	12	22	79	99	187
^1D	^1D	$1/11$	288	528	−209	1089	−605
	^1G	$(66)^{1/2}/11$	17	23	−11	−2	61
^1G	^1G	$(22)^{1/2}/121$	990	198	−270	873	54
	^1I	$(3003)^{1/2}/1573$	1430	286	−65	1378	79
^1I	^1I	$(143)^{1/2}/1573$	0	0	11 375	4095	35
^3P	^3P	$(21)^{1/2}/33$	0	0	−405	−297	891
	^3F	$(7)^{1/2}/44$	120	−88	420	0	−1452
^3F	^3F	$(294)^{1/2}/99$	270	−198	30	99	66
	^3H	$(462)^{1/2}/99$	135	−99	−105	−252	−69
^3H	^3H	$(3003)^{1/2}/1287$	0	0	−975	−1989	−39
		G[b]	$(726)^{1/2}/17\,640$	$(33)^{1/2}/3528$	$(726)^{1/2}/35\,280$	$(6)^{1/2}/10\,584$	$(6)^{1/2}/7056$

[a] The numbers F are multiplying factors common to all entries in a row.

[b] The numbers G are multiplying factors common to all entries in a column.

estimation of the effect of configuration interaction with these wave functions, we are reluctant to use them in this way. As she pointed out, the perturbing effects of configurations other than $4f\,5f$ and $4f\,6p$ may produce a very important cumulative effect.

In the absence of a firm *ab initio* criterion to select the operators $\vec{S}^{(k)}$ which are most important, we have used a criterion that is suggested by the first-order analyses. We have selected all of those operators which join the $^1D_2$ state to itself, i.e., those two-body operators having a tensor structure ^1D and ^1G. This includes all of the p excitation operators, and six of the twelve f excitation operators. Since the $^1D_2$ is especially sensitive to configuration interaction, it is reasonable to expect that these operators together represent a large part of the effect.

IV. MATRIX ELEMENTS

The matrix elements of $\vec{S}^{(k)}$ are given by[16]

$$\begin{aligned}(l^n\gamma SLJ\|\vec{S}^{(k)}\|l^n\gamma' S'L'J') &= \delta(S,S')(-)^{S+L'+J+k}[(2J+1)(2J'+1)]^{1/2} \\ &\times \begin{Bmatrix} L & k & L' \\ J' & S & J \end{Bmatrix} (l^n\gamma SL\|\vec{S}^{(k)}\|l^n\gamma' SL'). \qquad (4)\end{aligned}$$

One method of calculating reduced matrix elements for a configuration l^n is to relate them to the reduced matrix elements of l^{n-1} through the equation[16]

$$\begin{aligned}(l^n\psi\|\vec{S}^{(k)}\|l^n\psi') &= \delta(S,S')[N/(N-2)] \\ &\times[(2L+1)(2L'+1)]^{1/2}\sum(\psi\{|\bar{\psi})(\psi'\{|\bar{\psi}') \\ &\times(-)^{\bar{L}+l+L'}\begin{Bmatrix} L & k & L' \\ \bar{L}' & l & \bar{L}\end{Bmatrix}(l^{n-1}\bar{\psi}\|\vec{S}^{(k)}\|l^{n-1}\bar{\psi}'), \qquad (5)\end{aligned}$$

where the sum runs over the parent states $\bar{\psi}$ and $\bar{\psi}'$ of l^{n-1}. Thus, all the reduced matrix elements for f electrons can be obtained by a chain calculation once those for the starting configuration f^2 are specified. The matrix elements of $\vec{S}^{(2)}$ for the configuration f^2 are given in Table IV.

The evaluation of matrix elements using Eq. (5) becomes a tedious prospect for configurations f^N in which $N \geq 3$. Although the configuration interaction mechanism, which we have considered, should be the most important, there are other processes, which may also have a significant effect. An example is the third-order process in which two $4f$ electrons are excited to the $5d$ shell by means of the Coulomb interaction and interact within the configuration $f^{n-2}d^2$ by means of the crystal field. Any perturbative mechanism – other than the one we have considered – will usually lead to different effective operators whose matrix elements must also be calculated. Thus, it is convenient to introduce a complete set of operators in terms of

TABLE V. Description of operators.

$\vec{X}^{(2)}_1$	$^5(1111000)$	(220)	(20)	^1D
$\vec{X}^{(2)}_2$	$^5(1111000)$	(220)	(21)	^1D
$\vec{X}^{(2)}_3$	$^5(1111000)$	(220)	(22)	^1D
$\vec{X}^{(2)}_4$	$^1(2200000)$	(400)	(40)	^1D
$\vec{X}^{(2)}_5$	$^1(2200000)$	(220)	(20)	^1D
$\vec{X}^{(2)}_6$	$^1(2200000)$	(220)	(21)	^1D
$\vec{X}^{(2)}_7$	$^1(2200000)$	(220)	(22)	^1D
$\vec{X}^{(2)}_8$	$^1(2200000)$	(200)	(20)	^1D
$\vec{X}^{(2)}_9$	$^1(1100000)$	(200)	(20)	^1D
$\vec{X}^{(2)}_{10}$	$^3(1100000)$	(200)	(20)	^1D
$\vec{X}^{(2)}_{11}$	$^5(1100000)$	(200)	(20)	^1D

TABLE VI. The matrix elements $(\psi \mid \vec{X}_i^{(2)} \mid \psi')$.

ψ	ψ'	F	$\vec{X}_1^{(2)}$	$\vec{X}_2^{(2)}$	$\vec{X}_3^{(2)}$	$\vec{X}_4^{(2)}$	$\vec{X}_5^{(2)}$	$\vec{X}_6^{(2)}$	$\vec{X}_7^{(2)}$	$\vec{X}_8^{(2)}$	$\vec{X}_9^{(2)}$	$\vec{X}_{10}^{(2)}$	$\vec{X}_{11}^{(2)}$
^1S	^1D	$\frac{\sqrt{42}}{11}$	0	0	0	0	0	0	0	0	− 16 + 16	− 2	− 10 − 5
^1D	^1D	$\frac{1}{11}$	181	264	11	33	543	264	11	231	11(8 − 1)	11	11(5 − 1)
	^1G	$\frac{\sqrt{66}}{11}$	18	− 13	− 2	1	54	− 13	− 2	− 42	− 2(8 − 1)	− 2	− 2(5 − 1)
^1G	^1G	$\frac{\sqrt{22}}{11^2}$	− 24	− 1224	40	36	− 72	− 1224	40	− 189	− 9(8 − 1)	− 9	− 9(5 − 1)
	^1I	$\frac{\sqrt{3003}}{1573}$	− 546	182	− 14	49	− 1638	182	− 14	− 546	− 26(8 − 1)	− 26	− 26(5 − 1)
^1I	^1I	$\frac{\sqrt{143}}{1573}$	455	2184	217	− 105	1365	2184	217	− 9555	− 455(8 − 1)	− 455	− 455(5 − 1)
^3P	^3P	$\frac{\sqrt{21}}{33}$	− 21	0	− 11	0	231	0	121	− 1089	9(8 − 1)	+9	9(5 − 1)
	^3F	$\frac{\sqrt{7}}{44}$	− 64	264	0	0	704	− 2904	0	+2904	− 24(8 − 1)	− 24	− 24(5 − 1)
^3F	^3F	$\frac{7\sqrt{6}}{99}$	− 112	0	0	0	1232	0	0	− 363	3(8 − 1)	+3	3(5 − 1)
	^3H	$\frac{\sqrt{462}}{99}$	− 16	− 81	0	0	176	891	0	+726	− 6(8 − 1)	− 6	− 6(5 − 1)
^3H	^3H	$\frac{\sqrt{3003}}{1287}$	91	0	− 27	0	− 1001	0	297	+4719	− 39(8 − 1)	− 39	− 39(5 − 1)

which any two-body operator, having a tensor structure ^1D, ^1G, or ^1I, can be expressed.

A set of operators $\vec{X}_i^{(2)}$ which serve as a basis for those two-body operators having a rank zero in the spin space and a rank 2 in the orbital space are described in Table V. These operators transform according to definite representations of the continuous groups Sp_{14}, R_7, and G_2, introduced by Racah.[17] They also have a quasispin rank (K). Thus, matrix elements of $\vec{X}_i^{(2)}$ for the configuration f^{14-N} may readily be obtained from those of f^N. In Racah's phase convention, operators having an even quasispin rank are the same for f^{14-N} and f^N, while operators having an odd quasispin rank change sign. Methods for obtaining the matrix elements of operators, which have well-defined group-theoretical properties, and methods for decomposing other operators in terms of them have been described by Judd.[18,4] The matrix elements of $\vec{X}_i^{(2)}$ are given in Table VI, and in Table VII the operators $\vec{S}^{(2)}$ are expressed in terms of them. The operators $\vec{X}_9^{(2)}$ and $\vec{X}_{11}^{(2)}$ have both one-body and two-body parts (the one-body part is given first in Table VII); the operator $\vec{X}_{10}^{(2)}$ is a pure one-body operator. Since the operators $\vec{S}^{(2)}$ are pure two-particle operators, the one-particle parts cancel out when the sums in Table VII are performed; but it is necessary to introduce them into $\vec{X}_9^{(2)}$, $\vec{X}_{10}^{(2)}$, and $\vec{X}_{11}^{(2)}$ if these operators are to have definite quasispin ranks.

Equation (5) can be used to obtain the matrix elements of the operators $\vec{X}_i^{(2)}$ for configurations f^N for which $N > 2$. Since these operators have been classified according to the same groups which have been used to define the states, the Wigner-Eckart theorem may be used for the higher groups. In this way whole classes of seemingly unrelated matrix elements may be shown to be proportional. In practical terms, this means that for a given number of electrons enough general conditions are available to check the matrix elements of $\vec{X}_i^{(2)}$ thoroughly. The matrix elements of the operators $\vec{S}^{(2)}$ may then be obtained by using Table VII. A similar analysis can, of course, be employed for the operators $\vec{S}^{(4)}$ and $\vec{S}^{(6)}$.

V. COMPARISON WITH EXPERIMENT

As we mentioned earlier, the inclusion of the electrostatic crystal-field interaction introduces five new parameters, and our treatment of configuration interaction introduces another ten. However, the number of experimental levels used in the fitting procedure has been increased from the 12 centers of gravity of the "free-ion" analysis, to the 41 Stark levels of $LaCl_3 : Pr^{3+}$ identified by Dieke and Sarup.[13] The results of fitting the Stark levels using these additional parameters are summarized in the last two columns of Table II.

All of the parameters which correspond to the

TABLE VII. Decomposition of operators $\vec{S}^{(2)}$ into group-theoretical parts.

$\vec{S}^{(2)}_{p2}$	$(726)^{1/2}/17640$	$[-(60/49)\vec{X}^{(2)}_1-(5/18)\vec{X}^{(2)}_2+(52/3)\vec{X}^{(2)}_4+(6/49)\vec{X}^{(2)}_5+(5/126)\vec{X}^{(2)}_6$ $+2\vec{X}^{(2)}_9-36\vec{X}^{(2)}_{10}+4\vec{X}^{(2)}_{11}]$
$\vec{S}^{(2)}_{p4}$	$(33)^{1/2}/3528$	$[(44/49)\vec{X}^{(2)}_1+(11/54)\vec{X}^{(2)}_2+(104/9)\vec{X}^{(2)}_4-(22/245)\vec{X}^{(2)}_5-(11/378)\vec{X}^{(2)}_6$ $-(14/355)\vec{X}^{(2)}_8+(242/213)\vec{X}^{(2)}_9-(374/71)\vec{X}^{(2)}_{10}-(814/1065)\vec{X}^{(2)}_{11}]$
$\vec{S}^{(2)}_{f2}$	$(726)^{1/2}/35280$	$[-(55/392)\vec{X}^{(2)}_1+(5/9)\vec{X}^{(2)}_2+(455/32)\vec{X}^{(2)}_3-(26/3)\vec{X}^{(2)}_4$ $+(11/784)\vec{X}^{(2)}_5-(5/63)\vec{X}^{(2)}_6-(65/32)\vec{X}^{(2)}_7-(7/71)\vec{X}^{(2)}_8$ $+(1457/213)\vec{X}^{(2)}_9-(6047/71)\vec{X}^{(2)}_{10}+(1297/213)\vec{X}^{(2)}_{11}]$
$\vec{S}^{(2)}_{f4}$	$(6)^{1/2}/10584$	$[-(33/196)\vec{X}^{(2)}_1+(2/3)\vec{X}^{(2)}_2+(273/16)\vec{X}^{(2)}_3+26\vec{X}^{(2)}_4+(33/1960)\vec{X}^{(2)}_5$ $-(2/21)\vec{X}^{(2)}_6-(39/16)\vec{X}^{(2)}_7-(63/355)\vec{X}^{(2)}_8+(363/71)\vec{X}^{(2)}_9$ $-(1683/71)\vec{X}^{(2)}_{10}-(1221/355)\vec{X}^{(2)}_{11}]$
$\vec{S}^{(2)}_{f6}$	$(6)^{1/2}/7056$	$[(11/56)\vec{X}^{(2)}_1-(7/9)\vec{X}^{(2)}_2-(637/32)\vec{X}^{(2)}_3-(14/3)\vec{X}^{(2)}_4-(11/560)\vec{X}^{(2)}_5$ $+(1/9)\vec{X}^{(2)}_6+(91/32)\vec{X}^{(2)}_7-(119/355)\vec{X}^{(2)}_8+(2057/213)\vec{X}^{(2)}_9$ $-(3179/71)\vec{X}^{(2)}_{10}-(6919/1065)\vec{X}^{(2)}_{11}]$

excitation of an electron to a higher-lying orbital by means of the crystal field were well determined except $R^{(2)}_{p4}$ and $R^{(4)}_{p2}$. The values of the crystal-field parameters obtained in this fit and the calculated parameters of Ellis and Newman[19] are given in the last three rows of Table III.

One interesting feature of this fit is the large change of the crystal-field parameter A^6_6 when configuration interaction is added explicitly, $\delta A^6_6 = 227$. The value which A^6_6 assumes when configuration interaction is absorbed by other parameters lies between the two values of Ellis and Newman, and by itself does not offer a good test of the importance of charge penetration and covalency. The largest relative contribution of charge penetration and covalency which they obtained was for the parameter A^2_0. This agrees qualitatively with the analysis of absorption intensities of rare-earth ions in solution.[20] Of the coefficients of $\vec{U}^{(\lambda)}$ in Judd's formula,[21] that of $\vec{U}^{(2)}$ is the most sensitive to changes in the environment of the rare-earth ion. Apart from the parameter A^6_0, the final values of the crystal-field parameters which we obtain are uniformly smaller than the values which Ellis and Newman obtain with charge penetration and covalency.

VI. CONCLUSION

We have seen that by introducing two-body operators, which represent the excitation of a $4f$ electron to a higher-lying p or f orbital by means of the crystal field, a considerable improvement in the fit of the Stark levels of $LaCl_3$: Pr^{3+} can be obtained. When the effect of configuration interaction is absorbed by these new parameters, the ordinary crystal-field parameters change by a small but significant amount.

It is our view, however, that a similar parametric fit of the Stark levels of configurations f^N for which $N \geq 3$, should await a Hartree-Fock estimate of the relative importance of third-order crystal-field interactions.

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