Energy Levels of Tetragonally Sited Pr^{3+} Ions in Calcium Fluoride Crystals

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The crystal-field-split levels of tetragonally sited Pr^{3+} ions in calcium fluoride crystals have been experimentally determined and the crystal field constants have been calculated as $B_0^2 = 500$, $B_0^4 = -350$, $B_0^6 = 600$, $B_4^4 = 200$, and $B_4^6 = 550$. From center-of-gravity values of the experimental levels, and using a constant electrostatic depression of 1200 cm⁻¹ for all levels with energies over 10 000 cm⁻¹, the multiplet-level solution has been determined as it exists in the crystal field. Parameters determined for that multiplet solution are $F_0 = 13828$, $F_2 = 324$, $F_4 = 58.0$, $F_6 = 6.01$, and $\zeta = 770$. New positions in crystal fields of the ^3P and ^1I multiplets have been established, with centers of gravity being approximately 20 830 cm⁻¹ for $^3P_1$, 21 470 cm⁻¹ for $^1I_6$, and 22 640 cm⁻¹ for $^3P_2$.

I. INTRODUCTION

The f^2 inner-shell electron system can be very useful in assessing theoretical approaches to energy-level calculations. This system of 13 multiplet levels, involving 91 electron states, is sufficiently complex to allow generalization of analysis results, and yet is adequately simple to be readily amenable to theoretical and experimental study. Also, the solution for the gaseous Pr^{3+} free ion has been experimentally determined,[1,2] allowing a monitoring of conclusions arrived at for the ion system.

An earlier report[3] presented a solution for the f^2 tetravalent uranium ion in trigonal sites in calcium fluoride single crystal. The present report concerns trivalent praseodymium ions in tetragonal sites in the same crystal. An important aspect of the work involved the growing of CaF_2 : 1.0-mol% Pr^{3+} crystals under high-vacuum conditions, with adequate F⁻ ions present during growth, to allow the establishment of almost entirely tetragonal sites. Some weak "other-site" absorptions were seen, but they were eliminated from consideration by direct comparisons with absorptions seen in crystals having stronger other-site transitions.

Rather complex theoretical treatments have been evolving in recent years which increasingly define the importance of various second-order effects determining energy-level positions.[4] The results of the present report indicate that such treatments have in the past been incorrectly applied to various studies of the Pr^{3+} ion in crystals, and probably sometimes to other systems also. The extra degrees of freedom allowed by the second-order corrections have permitted a forced correlation of calculated and experimental crystal-field-split levels to an unjustified accuracy. The following reasons are given as a basis of this conclusion.

(i) There has been an incorrect identification of the crystal-field-split levels of the $^3P_0$, $^3P_1$, and $^1I_6$ multiplets of Pr^{3+}.

`(ii) The f^2 crystal field matrix elements *in R-S coupling* derive directly from symmetry and orbital properties, not on multiplet total-energy positions. In the Pr^{3+} multiplets $^3H_5$, $^3F_3$, and $^3P_1$, as well as in the almost 100% unmixed $^3H_6$ and $^1I_6$ multiplets, it can readily be shown by crystal field matrix calculations that considerable discrepancies between calculated and experimental crystal-field-split levels are inevitable, if the same B_q^k crystal field constants are assumed for all multiplets.

(iii) The simple form of the $\alpha L(L+1)$ correction was developed by Trees to explain transition-ion spectra,[5] but the correction does not appear to apply as a major factor in calculations involving Pr^{3+} ions in crystal solution. There is no similar appearance here of consistent L-related deviations.

In view of the above discussion, some minor changes in calculation techniques are involved in the solutions as presented. Use is made of the Slater integrals and the Spedding intermediate-coupling solutions, with emphasis on the low-energy terms $^3H_5$ and $^3F_3$ defining a nonhydrogenic value of F_6 in the Slater integrals. This is done via Eqs. (1)–(4) of the earlier report.[3] In this treatment, the Trees α constant becomes near zero for the solution of the gaseous free ion Pr^{3+}. However, in the crystal field solution the Trees correction is not used, and instead a constant 1200-cm⁻¹ deduction from all electrostatic energy values above 10 000 cm⁻¹ has been found to yield a reasonably good correlation of experimental and calculated multiplet energy-level positions.

II. EXPERIMENTAL RESULTS

Optical absorption studies were carried out with the spectroscopic equipment described previously.[3] All of the multiplets of Pr^{3+} except $^1S_0$ were studied in the infrared and visible spectral regions. Energy values of crystal-field-split levels were determined for a crystal temperature of 20 °K, but

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TABLE I. Crystal-field-split levels in cm^{-1} (vacuum) of tetragonally sited Pr^{3+} ions in calcium fluoride single crystals at 20 °K. Crystal field constants are $B_0^2 = 500$, $B_0^4 = -350$, $B_0^6 = 600$, $B_4^4 = 200$, and $B_4^6 = 550$.

Multiplet	Energy and degeneracy — Expt. (cm^{-1}; offset, symmetry; absolute)	Energy and degeneracy — Calc. (cm^{-1}; offset, symmetry)
$^3H_4$	0 B_1; 35 B_2; 83 A_1; 99 E; 134 E; 154 A_1; 208 A_2	0 B_1; 36 B_2; 58 A_1; 61 E; 141 E; 259 A_1; 262 A_2
$^3H_5$	0 B_1 (2179); 54 B_2 (2233); 118 E (2297); 136 E (2315); ⋯; ⋯; ⋯; 202 E (2381)	0 B_1; 6 B_2; 21 E; 23 E; 28 A_2; 123 A_1; 126 A_2; 205 E
$^3H_6$	0 E (4268); 13 B_1 (4281); 19 B_2 (4287); 52 E (4320); 67 A_1 (4335); ⋯; ⋯; ⋯; 259c B_2 (4527c)	0 E; 5 B_1; 6 B_2; 54 E; 55 A_1; 57 A_2; ⋯; ⋯; 259 B_2
$^3F_2$	0 B_1 (5208); 11 B_2 (5219); 24 E (5232); 163 A_1 (5371)	0 B_1; 12 B_2; 43 E; 71 A_1
$^3F_3$	0 B_1 (6456); 63 E (6519); ⋯ (⋯); 193 B_2 (6649); 262 E (6718)	0 B_1; 12 E; 43 A_2; 62 B_2; 86 E; 103 A_2; 120 B_2
$^3F_4$	0 E (6915); 167 B_1 (7072); 270 A_1 (7185); 317 A_2 (7232)	0 E; 28 B_1; 51 A_1; 57 A_2; 90 E; 103 A_2; 120 B_2
$^1G_4$	0c A_1 (⋯); 18 E (9794); 284 B_1 (10060); 376 E (10152)	0 A_1; 18 E; 32 B_1; 110 E; 158 A_1; 165 A_2; 228 B_2
$^1D_2$	0 B_1 (16873); 42 B_2 (16915); 117 A_1 (16990); 179 E (17052)	0 B_1; 74 B_2; 144 A_1; 185 E
$^3P_1$	0 A_2 (20754c); 110 E (20864)	0 A_2; 110 E
$^1I_6$	0 A_1 (21354); 38 E (21392); 46 B_2 (21400); 63 B_1 (21417); 72 E (21426); 108 A_1 (21462); 165 E (21519); 222 B_1 (21576); 433c B_2 (21787c)	0 A_1; 38 E; 119 B_1; 124 B_2; 230 E; 314 A_1; 315 A_2; 369 E; 429 B_1; 433 B_2
$^3P_2$	0 A_1 (22560); 11 B_1 (22571); 15 B_2 (22575); 182 E (22742)	0 B_1; 8 B_2; 120 E; 148 A_1

studies were made at higher temperatures to determine levels involving weak transitions at 20 °K. All transitions were found to obey electric-dipole selection rules for tetragonal symmetry, which allow transitions B_1 to B_1, B_2 to B_2, A_1 to A_1,

A_2 to A_2, and all transitions to or from doublet E levels to singlet levels. No polarization occurs in the spectra owing to the averaging effect of three mutually perpendicular tetragonal axes.

When levels could not be determined experimen-
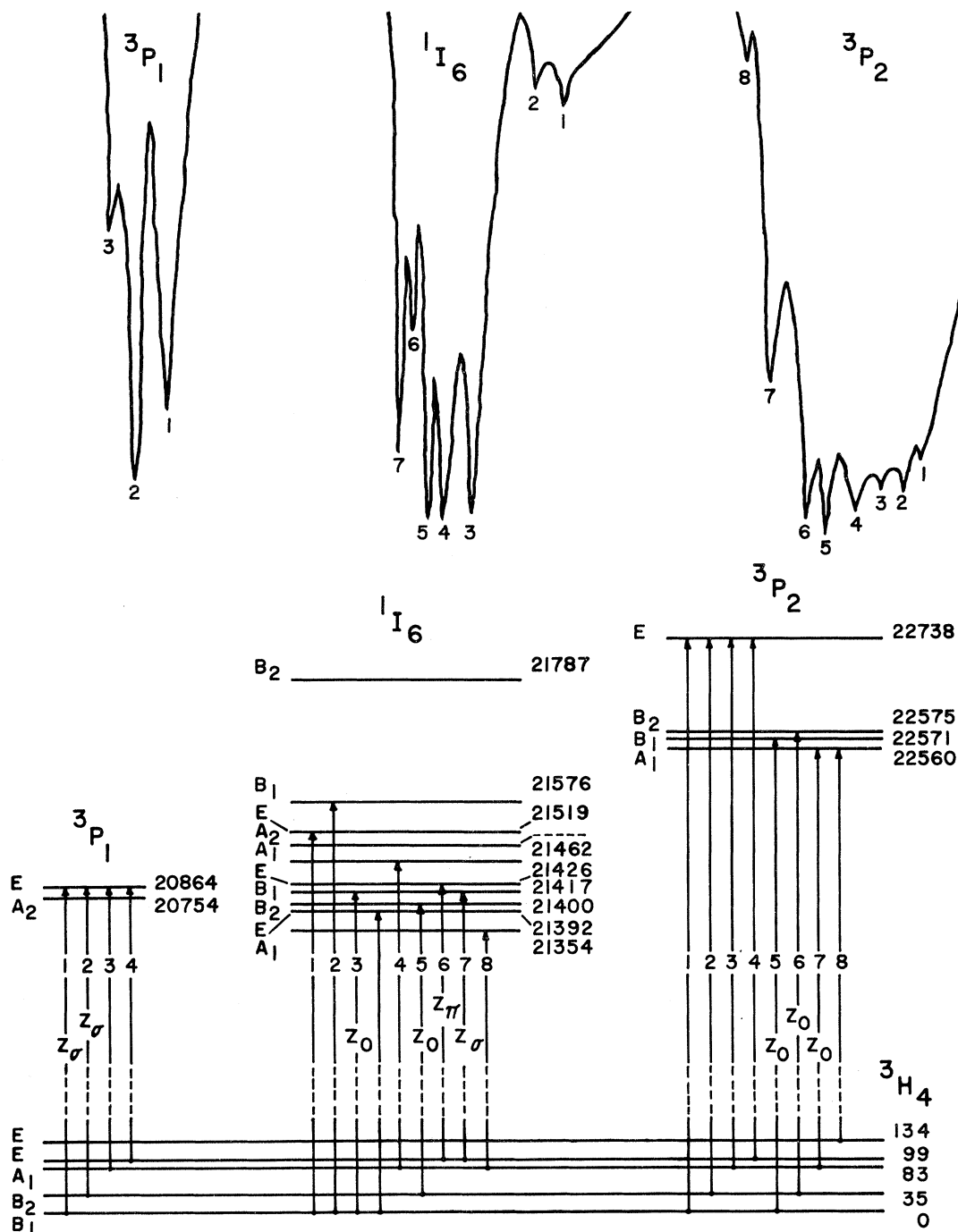
FIG. 1. Crystal-field-split optical-absorption spectra of $^3P_1$, $^1I_6$, and $^3P_2$ multiplets of tetragonally sited CaF$_2$: Pr^{3+} at 77 °K, and diagrams for these transitions. Zeeman confirmations are indicated by Z_0 (no Zeeman splitting), Z_σ (σ-polarized Zeeman-split transitions), and Z_π (π-polarized Zeeman-split transitions).

TABLE II. Off-diagonal matrix elements in tetragonal symmetry.

J	$\pm q$	k	$\langle 2\|\|-2\rangle$	$\langle 3\|\|-1\rangle$	$\langle 4\|\|0\rangle$	$\langle 5\|\|1\rangle$	$\langle 6\|\|2\rangle$
2	4	4	+0.3333	...	...	...	...
3	4	4	+0.2247	+0.1741	...	...	...
3	4	6	−0.2048	+0.1322	...	...	...
4	4	4	+0.1870	+0.1649	+0.1043	...	...
4	4	6	−0.1399	−0.0264	+0.1672	...	...
5	4	4	+0.1649	+0.1527	+0.1183	+0.0683	...
5	4	6	−0.1176	−0.0590	+0.0703	+0.1521	...
6	4	4	+0.1496	+0.1419	+0.1199	+0.0868	+0.0475
6	4	6	−0.1044	−0.0688	+0.0184	+0.1061	+0.1291

tally, as a result of selection-rule prohibitions or of weak-transition probabilities, the calculated values were used to fill in the missing levels, with energy values followed by the letter c, which denotes calculated values.

Zeeman studies were carried out for the $^3P_1$, $^1I_6$, and $^3P_2$ multiplets in the visible region. The Zeeman field was applied along a tetragonal axis at crystal temperatures of 4 and 77 °K, and optical absorption was photographed along a perpendicular crystal path. In the Zeeman data presented in Fig. 1, singlet-to-singlet transitions were denoted by Z_0, indicating no Zeeman splitting; singlet-to-doublet transitions, being σ polarized, are denoted by Z_σ; and doublet-to-doublet transitions are denoted by Z_π. The Zeeman spectra usually showed an undeviated line as a result of the three tetragonal axes being present.

Figure 1 shows the absorption spectra, deduced level structure, and Zeeman confirmations for the tetragonal Pr^{3+} multiplet levels $^3P_1$, $^1I_6$, and $^3P_2$. Table I gives the experimental and calculated levels of all multiplets, with the exception of $^1S_0$, which was not studied.

III. CRYSTAL FIELD CALCULATIONS

In tetragonal symmetry the interactions involve changes in J_z of 0 or ±4, which are allowed q values. The $q=0$ values are given in Table III of the earlier report,[3] where the values are the same for U^{4+} and Pr^{3+} ions. For the tetragonal symmetry of Pr^{3+}, the $q=\pm4$ matrix values were calculated from standard tables and are given for possible J_z and k values in Table II. The intermediate-coupling matrix multipliers applying to group-theory calculations (proportional to operator equivalent multipliers in spherical harmonic treatment) are

given in Table III.

The experimental absorption transitions shown in Fig. 1, and all those detailed in Table I, follow selection-rule requirements, and in general their strengths fulfill predictions based on the proximity of the originating $^3H_4$ levels to the ground-zero level. With a fixed set of B_q^k crystal field constants for all multiplets, there is a good correlation between calculation and experiment of the *ordering* of crystal-field-split levels. In all ^3F multiplets the same is true, but the spread or span of crystal-field-split levels is about three times too much. This is the worst correlation seen and is true of the R-S $^3F_3$ multiplet as well as of the others. Much closer agreement in level positions was obtained in trial calculations where the B_q^k constants were allowed to vary between manifolds, but emphasis on qualitative results with a fixed set of B_q^k constants seemed to be suitable to the purposes of the present report.

IV. MULTIPLET-LEVEL CALCULATIONS

Table IV gives the results of iterative multiplet-level and crystal field calculations to define the multiplet-level system of tetragonally sited Pr^{3+} ions in calcium fluoride crystals. These are based on center-of-gravity values as they exist in the crystal field, and the constants used in deriving them are strictly related to the ion as it exists in the crystal field. Also in Table IV are the calculated percentage compositions of the various multiplets, the experimental multiplet positions as determined by center of gravity of crystal-field-split levels, and the experimental free-ion levels of gaseous Pr^{3+}.

V. DISCUSSION OF RESULTS

As shown in Fig. 1, the present results change considerably the energy positions of the $^3P_0$, $^3P_1$, and $^1I_6$ multiplets of Pr^{3+} in crystal solution from all previous reports. Contrary to the spin-resonance results of Wetsel et al.,[6] there is not a doublet ground-zero level in the tetragonally sited Pr^{3+} ion system, and a contamination of their crystal by sites other than tetragonal is indicated. The absence of a doublet at ground-zero level is shown by all of the results of the present study, but it is particularly emphasized by the Zeeman data, which show two strong Z_σ transitions in $^3P_1$, strong Z_σ lines in $^1I_6$, and all three strong lines in

TABLE III. Intermediate-coupling multipliers for $CaF_2 : Pr^{3+}$, tetrag.

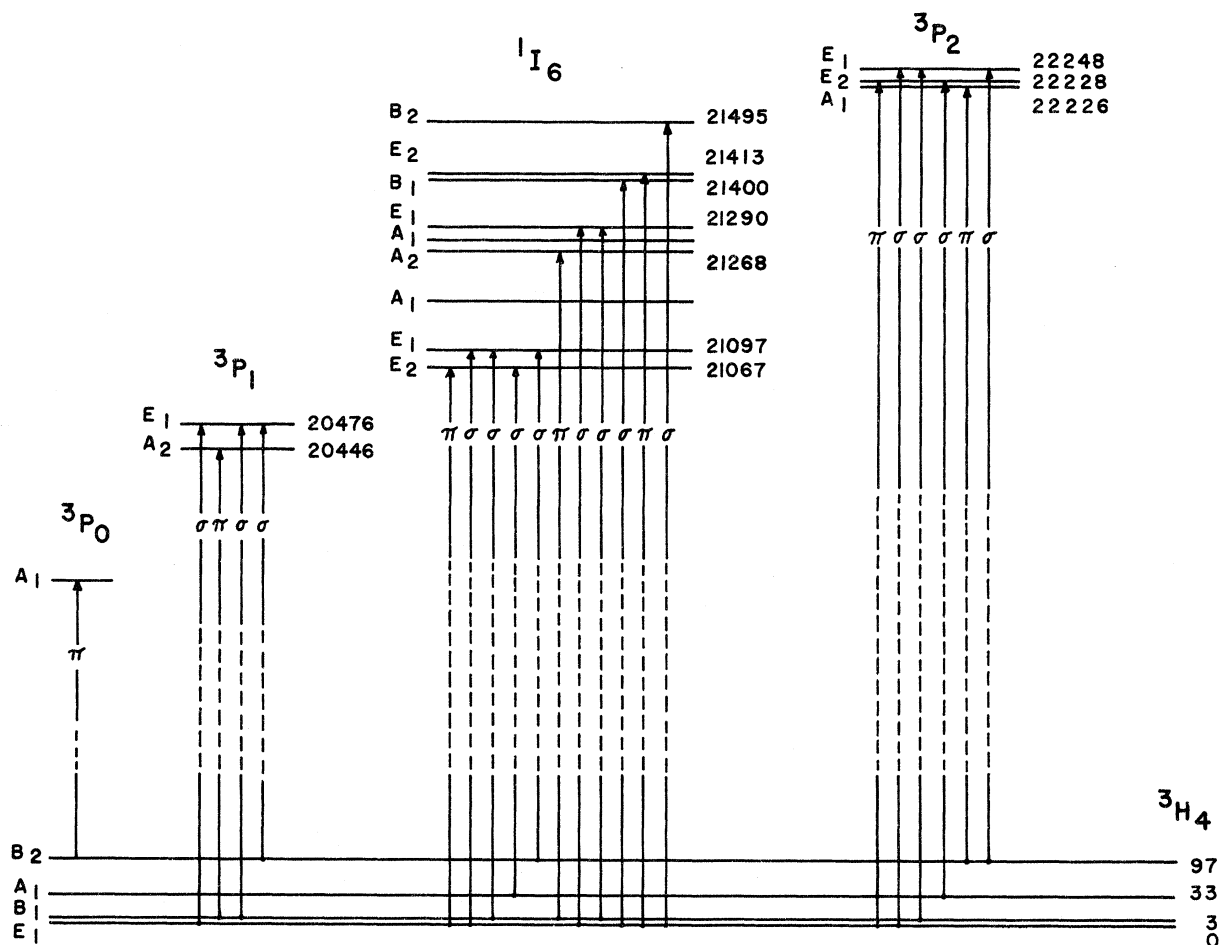| k value	$^3F_2$	$^3P_2$	$^1D_2$	$^3H_4$	$^3F_4$	$^1G_4$
2	−0.2430	−0.6150	−0.6092	+0.8886	−0.1450	+0.0336
4	−0.0979	+0.0661	+0.5619	−0.6658	−0.5428	−0.7891
6	0.0000	0.0000	0.0000	−0.5597	+0.3375	+0.8136

FIG. 2. Reinterpretation of absorptive transitions to the crystal-field-split levels of the ^3P and $^1I_6$ multiplets of $LaCl_3 : Pr^{3+}$ in D_{3h} symmetry, from data of Sayre, Sancier, and Freed, and proposed new level identifications.

$^3P_2$ being no-splitting lines Z_0. There are no strong Z_r lines in $^3P_1$, $^1I_6$, or $^3P_2$, which would occur with a ground-zero doublet in $^3H_4$.

Instead of earlier problems of separating a mixed $^3P_1-^1I_6$ group of crystal-field-split levels, we have in $CaF_2 : Pr^{3+}$ tetragonal crystal two clearly separated manifolds. The A_2 level of $^3P_1$ is not determined by an absorptive transition, since there is no near-ground A_2 level in $^3H_4$. Also, the $^3P_0$ multiplet has not been seen, for a similar reason, there being no strongly allowed transition from a near-ground level.

Discussion of the correlation of these new data with those of previous reports is taken up in the Appendix.

APPENDIX

Most of the published interpretations of Pr³⁺ crystal-field-splitting spectra relate to the interpretation of Sayer, Sancier, and Freed of absorption spectra of Pr³⁺-doped lanthanum chloride

crystals.[7] A photograph of the Sayre *et al.* data for the ^3P multiplet, given in an article by McClure,[8] is clear and useful for study. A reinterpretation of these data, in view of the results of the present report, is shown in Fig. 2.

Changes are made in the level identifications of the $^3H_4$ multiplet; in particular, a doublet E_2 zero-ground-state level becomes a doublet E_1 level. Using D_{3h} selection rules, the transition E_1 to A_1 is not allowed. There is no transition from ground zero or from any other level near ground zero to $^3P_0$, and the position of $^3P_0$ is not determined from absorptive transitions. In similarity to the $CaF_2 : Pr^{3+}$ system, the $^3P_1$ multiplet, in the new interpretation of the Sayre *et al.* data, is placed in the 20 460-cm⁻¹ region, and $^1I_6$ is placed in the 21 260-cm⁻¹ region. A careful calibration of the strong and weak lines in the McClure photograph (Fig. 19 of Ref. 8) has permitted a development of the $^1I_6$ manifold, as shown in Fig. 2 of this work, with all lines compatible with D_{3h} selection-rule require-

TABLE IV. Multiplet energy levels of Pr^{3+} in CaF_2, tetrag.

Multiplet	Calc.[a]	Composition[b]	Expt.[c]	Gaseous free ion[d]
$^3H_4$	162	97.6% $^3H_4$, 2.4% $^1G_4$	105	0
$^3H_5$	2 307	100% $^3H_5$	2 307	2 152
$^3H_6$	4 564	99.7% $^3H_6$, 0.3% $^1I_6$	4 367*	4 389
$^3F_2$	5 126	97.6% $^3F_2$, 2.4% $^1D_2$	5 252	4 997
$^3F_3$	6 570	100% $^3F_3$	6 595	6 415
$^3F_4$	7 122	65% $^3F_4$, 35% $^1G_4$	7 064*	6 855
$^1G_4$	10 244	63% $^1G_4$, 35% $^3F_4$, 2% $^3H_4$	10 040*	9 921
$^1D_2$	17 062	88% $^1D_2$, 2.4% $^3F_2$, 9.6% $^3P_2$	16 976	17 335
$^3P_0$	20 405	99.3% $^3P_0$, 0.7% $^1S_0$	...	21 390
$^3P_1$	21 002	100% $^3P_1$	20 827*	22 008
$^1I_6$	21 308	99.7% $^1I_6$, 0.3% $^3H_6$	21 474*	22 212
$^3P_2$	22 338	90.6% $^3P_2$, 9.4% $^1D_2$	22 636	23 161
$^1S_0$	54 177	99.3% $^1S_0$, 0.7% $^3P_0$	...	...

[a]Calculated energies in cm^{-1}, with the calculation based upon Eqs. (1)–(3) of Ref. 3, and a constant deduction of 1200 cm^{-1} from electrostatic values of energies above 10 000 cm^{-1}. Constants of the calculation are $F_0 = 13828$, $F_2 = 324$, $F_4 = 58.0$, $F_6 = 6.01$, and $\zeta = 770$.

[b]Compositions are from eigenvectors of calculated solution.

[c]Experimental energies in cm^{-1}, based on center-of-gravity values of crystal-field-split levels; asterisk indicates that some missing experimental levels were replaced by calculated levels.

[d]Data from Ref. 1.

ments.

Many related reports have been studied, with no contradiction of the new approach having been found. Paramagnetic spin-resonance studies by

Hutchison and Wong[9] on Pr^{3+} ions in $LaCl_3$ do not appear to offer a conflict, since the low experimental value of $g_{||} = 1.035$ would not be incompatible with the proposed ± 1 zero-ground level for $^3H_4$.

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Renormalization-Group Techniques in the Kondo Effect

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Various renormalization-type approaches to the Kondo problem are shown to be equivalent. It is pointed out that the exact solution to the ferromagnetic case has been known for many years in quantum field theory. For the antiferromagnetic case, in the infrared limit the effective coupling becomes infinite, and there is no "critical-exponent" behavior at zero energy. Some recent criticisms of Anderson scaling laws are discussed.

I. RENORMALIZATION METHODS

A standard approach to understanding a complex physical system is to attempt a description as a set of interacting elementary excitations. The Hamiltonian is written

$$H = H_0 + V ,$$

where H_0 is a diagonal matrix having as eigenstates the possible sets of independent elementary excitations and V describes the interaction between them. An example is the electron-phonon