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Electron-paramagnetic-resonance data interpretation for a $\Gamma_8(O_h)$ state in a cubic crystal field

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The electron-paramagnetic-resonance spectrum of an octahedral Γ_8 state is considered in general and particular attention is given to the angular dependent part of the Γ_8 behavior. It is shown that the experimentally reported angular dependence of the resonance field for Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6 with the external magnetic field $\vec{H}$ in the (111) plane is quantitatively explained by a Γ_8 spin Hamiltonian including only electronic Zeeman and nuclear hyperfine terms. Observed resonances in these two systems have been fit and spin Hamiltonian parameters g,g',A,A' have been determined. Zeeman parameters are employed to derive information about the relative importance of various orders in the crystal-field expansion and the hyperfine parameters for Pr^{2+}/CaF_2 are used to estimate the radial parameter $\langle r^{-3}\rangle$ for Pr^{2+}.

I. INTRODUCTION

During the course of an investigation into the electronic spectra of ReF_6 in pure and mixed crystals[1] an interesting EPR spectrum was obtained in the ReF_6/UF_6 system. At 4 K a complex, anisotropic spectrum that covers a range from 2000 to above 12000 G was observed. At higher temperatures (>30 K) the spectrum becomes isotropic with respect to the magnetic field direction, but the intensity pattern and the spacing of the lines are highly irregular. The observed spectra indicate a large Re hyperfine interaction. In addition, it is likely that fluorine superhyperfine interactions play an important role in the overall spectrum. Since it is known that there is a significant Jahn-Teller interaction in this octahedral system,[2] it seemed apparent that the temperature-dependent isotropic spectrum could arise from a motional process associated with the Jahn-Teller interaction. In other Jahn-Teller active paramagnetic $\Gamma_8(O_h)$ ground-state systems (e.g., Cu^{2+}/MgO,[3] V^{2+}/CaF_2,[4] La^{2+}/CaF_2,[5]) such motional averaging yields a high-temperature spectrum which can be fitted with an isotropic spin Hamiltonian. To date we have not been able to fit the highly irregular ReF_6/UF_6 spectrum to any isotropic spin Hamiltonian. In view of this difficulty we embarked on an investigation of the properties of the EPR spectra of Γ_8 states, in general.

The EPR spectrum of a Γ_8 state has been treated previously.[6–8] Perturbation expressions have been given for field-frequency relations but these presume that hyperfine interactions are small with respect to the Zeeman interaction. This is not the case in the ReF_6/UF_6 spectrum. Consequently, we have developed a program to calculate the EPR spectrum of a Γ_8 state rigorously. In using a complete diagonalization procedure for the Γ_8 spin Hamiltonian some interesting deviations from previously available perturbation results have been noted. Specifically, perturbation results predict that for rotation of the magnetic field $\vec{H}$ in a plane perpendicular to the (111) axis of a cubic crystal, there should be no angular dependence of the EPR spectrum. Notwithstanding there is indeed an angular dependence predicted in this plane based on a rigorously diagonalized Zeeman-hyperfine Hamiltonian, a result which is found to be in complete detailed agreement with observations for Pr^{2+} in CaF_2 (Ref. 9) and Np^{4+} in Cs_2ZrCl_6.[10] In fact, the previous reports have either not discussed the angular dependent Γ_8 state behavior, or have attributed it to noncubic perturbations. It is to this discrepancy that the current work is addressed.

We begin with a brief review of the spin Hamiltonian for an $O_h\Gamma_8$ state and the perturbation solution. We shall then proceed to a discussion of the difference between the perturbation result and the rigorous result. And finally we will discuss Zeeman and hyperfine parameters obtained in fitting published spectra for Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6.

II. Γ_8 SPIN-HAMILTONIAN THEORY

Bleaney[6] first treated the Γ_8 spin Hamiltonian. A more detailed treatement can be found in a series of papers concerned with Er^{3+} in MgO,[8] and in Abragam and Bleaney.[7] For convenience we reproduce the essentials of the theory here. Since in the O_h group $\Gamma_8\times\Gamma_8$ contains Γ_4 twice, the Cartesian components V_i of a vector $\vec{V}$ within a Γ_8 state may be represented by

$$V_i = aS_i + bS_i^3 \quad . \tag{1}$$

The nonvanishing matrix elements of V_z are

$$\begin{aligned}\langle\tfrac{3}{2}|V_z|\tfrac{3}{2}\rangle &= -\langle-\tfrac{3}{2}|V_z|-\tfrac{3}{2}\rangle = P \quad ,\\ \langle\tfrac{1}{2}|V_z|\tfrac{1}{2}\rangle &= -\langle-\tfrac{1}{2}|V_z|-\tfrac{1}{2}\rangle = Q \quad ,\end{aligned} \tag{2}$$

in which

$$P=\frac{3a}{2}+\frac{27b}{8} \quad \text{and} \quad Q=\frac{a}{2}+\frac{b}{8} \ . \tag{3}$$

The inverse of Eq. (3) gives

$$a=-\frac{P}{12}+\frac{9Q}{4} \quad \text{and} \quad b=\frac{P}{3}-Q \ . \tag{4}$$

The Γ_8 spin Hamiltonian including electronic Zeeman and magnetic hyperfine interactions may be written

$$\begin{aligned}\mathcal{H}=&\,g\mu_B\vec{S}\cdot\vec{H}+A\,\vec{S}\cdot\vec{I}\\&+g'\mu_B(S_x^3H_x+S_y^3H_y+S_z^3H_z)\\&+A'(S_x^3I_x+S_y^3I_y+S_z^3I_z)\end{aligned} \tag{5}$$

in which $g=\Lambda a$ and $g'=\Lambda b$ are respectively the linear and cubic g factors, Λ is the Lande g factor, and A and A' are respectively the linear and cubic magnetic hyperfine constants.

It is sometimes convenient to write

$$V_z=a'S_z+b[S_z^3-\tfrac{3}{5}(S(S+1))S_z+\tfrac{1}{5}S_z] \tag{6a}$$

in which

$$a'=a+\tfrac{1}{5}b[3(S(S+1))-1] \ . \tag{6b}$$

Using this latter formulation we may write for the spin Hamiltonian including Zeeman and magnetic hyperfine interactions

$$\begin{aligned}\mathcal{H}=g''\mu_B\vec{S}\cdot\vec{H}+A''\vec{S}\cdot\vec{I}+g'\mu_B\{S_x^3H_x+S_y^3H_y+S_z^3H_z-\tfrac{1}{5}(\vec{S}\cdot\vec{H})[3S(S+1)-1]\}&\\+A'\{S_x^3I_x+S_y^3I_y+S_z^3I_z-\tfrac{1}{5}(\vec{S}\cdot\vec{I})[3S(S+1)-1]\}&\ .\end{aligned} \tag{7}$$

Based on Eq. (7), the following perturbation result may be obtained for the energy levels of the system[7]:

$$W_{Mm}=g''\mu_BHM+A''Mm+(g'\mu_BH+A'm)\{M^3-\tfrac{1}{5}[3S(S+1)-1]M\}\delta \ , \tag{8}$$

with

$$\delta=\tfrac{5}{2}(n_1^4+n_2^4+n_3^4-\tfrac{3}{5}) \ .$$

The n_i are direction cosines of $\vec{H}$ with respect to the i axis. The result is derived under the assumption that the linear Zeeman term is large compared to the other terms.

Consider the angularly dependent term in Eq. (8). If $\vec{H}$ is rotated in a plane perpendicular to a (111) axis, δ is independent of angle and equal to $(-\frac{1}{4})$.[7,11] Thereby, based on the perturbation-theory result, EPR spectra of a Γ_8 quartet can be expected to be independent of the orientation of $\vec{H}$ for the case in which $\vec{H}$ is in the (111) plane, as noted by Bierig and Weber.[11] This perturbation result holds only for $g' \ll g''$.

III. RIGOROUS CALCULATION OF THE EPR SPECTRUM IN A Γ_8 STATE

The Zeeman interaction may be written in terms of the vector $\vec{V}$, whose components are given in Eq. (1), as

$$\mathcal{H}_z=\Lambda\mu_B\vec{V}\cdot\vec{H} \ . \tag{9}$$

The matrix elements for V_z are given in Eq. (2); V_x and V_y components are more complex. The procedure is to define V_x and V_y in terms of raising and lowering operators, in direct analogy to usual angular momentum algebra. Thus

$$\begin{aligned}V_x&=\tfrac{1}{2}(V_++V_-) \ ,\\V_y&=\frac{1}{2i}(V_+-V_-) \ ,\end{aligned} \tag{10}$$

with

$$V_+=a(S_x+iS_y)+b(S_x^3+iS_y^3) \tag{11}$$

and likewise for V_-. Using $S_x^3=[\frac{1}{2}(S_++S_-)]^3$ and $S_y^3=[(1/2i)(S_+-S_-)]^3$ along with commutation relations, we obtain after some algebra,

$$\begin{aligned}V_+&=V_+^{(1)}+V_+^{(3)}\\&=aS_++\tfrac{1}{4}b[S_-^3+3S_-S_+^2+2S_+(3S_z+2)] \ ,\end{aligned} \tag{12a}$$

$$\begin{aligned}V_-&=V_-^{(1)}+V_-^{(3)}\\&=aS_-+\tfrac{1}{4}b[S_+^3+3S_+S_-^2-2S_-(3S_z-2)] \ .\end{aligned} \tag{12b}$$

Matrix elements for the Zeeman interaction may then be calculated. These are given in Table I in terms of $g=\Lambda a$ and $g'=\Lambda b$. This problem is also conveniently solved by calculating the matrix elements of V_i in the Γ_8 basis in terms of P and Q.[8(a)] The resulting secular equation is given by

$$\begin{aligned}&y^4-(P^2+Q^2)y^2+P^2Q^2\\&\qquad+\tfrac{3}{16}(P-3Q)(3P-Q)(P+Q)^2\gamma \ ,\end{aligned} \tag{13}$$

with

$$\gamma=(n_1^2n_2^2+n_2^2n_3^2+n_1^2n_3^2) \ .$$

TABLE I. Matrix elements for the Zeeman interation in a Γ_8 state.

$\underline{\Delta M_s = 0}$

$$\langle M_s, M_I | \mathcal{H}_z | M_s, M_I \rangle = g\mu_B H_z M_s + g'\mu_B H_z M_s^3$$

$\underline{\Delta M_s = \pm 1}$

$$\begin{aligned}\langle M_s \pm 1, M_I | \mathcal{H}_z | M_s, M_I \rangle = {}& \tfrac{1}{2} g\mu_B (H_x \pm iH_y)[S(S+1) - M_s(M_s \pm 1)]^{1/2} \\ & + \tfrac{1}{8} g'\mu_B (H_x \pm iH_y)\{3[(S(S+1) - M_s(M_s \pm 1))^{1/2}(S(S+1) - (M_s \pm 1)(M_s \pm 2))] \\ & \pm 2(S(S+1) - M_s(M_s \pm 1))^{1/2}(3M_s \pm 2)\}\end{aligned}$$

$\underline{\Delta M_s + \pm 3}$

$$\begin{aligned}\langle M_s \pm 3, M_I | \mathcal{H}_z | M_s, M_I \rangle = {}& \tfrac{1}{8} g'\mu_B (H_x \mp iH_y)[(S(S+1) - M_s(M_s \pm 1)) \\ & \times (S(S+1) - (M_s \pm 1)(M_s \pm 2))(S(S+1) - (M_s \pm 2)(M_s \pm 3))]^{1/2}\end{aligned}$$

The angle dependent part of this equation is given by $\gamma = 1 - 5\delta$; that is, the rigorous solution for the Γ_8 electron Zeeman problem gives the same angular dependence as the approximate perturbation treatment. In this case the linear Zeeman interaction need not be large compared to the cubic Zeeman term.

We shall now consider the rigorous calculation of the hyperfine structure, with particular attention paid to the results it gives for a rotation of $\vec{H}$ in the (111) plane. The magnetic hyperfine interaction may be expressed as

$$\mathcal{H}_{HF} = \bar{A}\, \vec{V} \cdot \vec{I} \qquad (14)$$

in which $\vec{I}$ is the nuclear spin operator. This may be rewritten

$$\mathcal{H}_{HF} = A\, \vec{S} \cdot \vec{I} + A' \vec{S}^3 \cdot \vec{I} \ . \qquad (15)$$

If it is assumed that the vectors $\vec{V}$ for the hyperfine and Zeeman interaction are the same, then $A = a\bar{A}$ and $A' = b\bar{A}$. To proceed, we note that the V_+ operator in Eq. (12) has linear and cubic parts $V_+^{(1)}$ and $V_+^{(3)}$ respectively, and likewise for V_-. We may then write

$$\begin{aligned}\mathcal{H}_{HF} = {}& A\,[S_z I_z + \tfrac{1}{2}(V_+^{(1)} I_- + V_-^{(1)} I_+)] \\ & + A'[S_z^3 I_z + \tfrac{1}{2}(V_+^{(3)} I_- + V_-^{(3)} I_+)] \ . \qquad (16)\end{aligned}$$

Magnetic hyperfine matrix elements are calculated with this Hamiltonian [Eq. (16)] and are given in Table II.

TABLE II. Matrix elements for the magnetic hyperfine interaction in a Γ_8 state.

$\underline{\Delta M_s = 0, \ \Delta M_I = 0}$

$$\langle M_s, M_I | \mathcal{H}_{HF} | M_s, M_I \rangle = A M_s M_I + A' M_s^3 M_I$$

$\underline{\Delta M_s = \pm 1, \ \Delta M_I = \mp 1}$

$$\begin{aligned}\langle M_s \pm 1, M_I \mp 1 | \mathcal{H}_{HF} | M_s, M_I \rangle = {}& \tfrac{1}{2}\{A\,[S(S+1) - (M_s \pm 1)]^{1/2} \\ & + \tfrac{1}{4} A'\{3[(S(S+1) - M_s(M_s \pm 1))^{1/2}(S(S+1) - (M_s \pm 1)(M_s \pm 2))] \\ & \pm 2(S(S+1) - M_s(M_s \pm 1))^{1/2}(3M_s \pm 2)\}\}[I(I+1) - M_I(M_I \mp 1)]^{1/2}\end{aligned}$$

$\underline{\Delta M_s = \pm 3, \ \Delta M_I = \pm 1}$

$$\begin{aligned}\langle M_s \pm 3, M_i \pm 1 | \mathcal{H}_{HF} | M_s M_I \rangle = {}& \tfrac{1}{8} A'[(S(S+1) - M_s(M_s \pm 1))(S(S+1) - (M_s \pm 1)(M_s \pm 2))(S(S+1) - (M_s \pm 2)(M_s \pm 3)) \\ & \times (I(I+1) - M_I(M_I \pm 1))]^{1/2}\end{aligned}$$

We have written a program which sets up and solves the complete energy matrix for the full Γ_8 Hamiltonian [Eqs. (9) plus (15)]. The program can calculate the field swept or the frequency swept spectrum and output lists of lines and intensities along with plots of transition energies or energy levels. The magnetic field may be specified at any orientation. The field swept spectrum is difficult to calculate in some cases, however. EPR field swept resonances are obtained by taking an estimated field, calculating the frequency for the specified transition at the particular field, and then changing the field to bring the calculated transition frequency into coincidence with the experimental klystron frequency. Other transitions in the spectrum, not directly calculated, are estimated by linear extrapolation from calculations at magnetic fields that bracket the feature in question. This extrapolation procedure works well in some cases; for example, in calculating the spectrum of the Γ_8 ground state of the Er^{3+}/MgO system. In this system,[8(b),8(c)] which we used as a test case, the extrapolation procedure gave an accuracy on all lines of better than 0.004% (0.067 G) using only two fields to bracket the entire experimental spectrum. On the other hand, the extrapolation procedure failed for Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6, in which case every line had to be separately calculated. (See Sec. IV.) The problem in these latter two systems is associated with level crossings and anticrossings. Neither of these systems has yet reached the "high-field" limit at the experimental resonance condition.

Spin-Hamiltonian parameters may be fit to the experimental spectrum using a fitting routine patterned after that of Palmer *et al.*[12] The one drawback of this program is the expense of calculations for nuclear spins of $\frac{5}{2}$ or greater. On our CDC Cyber 171 computer it commonly takes 80 to 150 seconds to calculate 12 EPR lines for the $\Gamma_8(J=\frac{3}{2})$ state with nuclear spin $I=\frac{5}{2}$. The fitting routines turn out to be even more expensive. In general, to get a fit of the experimental data for systems in which the hyperfine interaction is large is not straightforward and involves several iterations.

IV. CALCULATIONS FOR Pr^{2+}/CaF_2 AND Np^{4+}/Cs^2ZrCl_6

A. Spin-Hamiltonian parameter

We have taken experimental resonance fields for Pr^{2+}/CaF_2 (Ref. 9) and Np^{4+}/Cs_2ZrCl_6 (Ref. 10) from figures in the respective papers, and attempted to fit the observed angular dependence. The procedure was first to fit the spectrum observed with $\vec{H}\parallel(001)$. In both systems under consideration, only one set of hyperfine lines is observed in this orientation, that being $|\frac{3}{2},I_z\rangle \leftrightarrow |-\frac{3}{2},I_z\rangle$, the $|\frac{1}{2},I_z\rangle \leftrightarrow |-\frac{1}{2},I_z\rangle$ set being out of the range of the magnet. Now for $\vec{H}\parallel(001)$ the $|-\frac{3}{2},I_z\rangle \leftrightarrow |\frac{3}{2},I_z\rangle$ lines are dependent on only P and the hyperfine parameters A and A'. With P fit, the spectrum is then calculated in some other orientation [e.g., $\vec{H}\parallel(101)$]. This gives a value for Q and for the hyperfine parameters. It was found that, in order to get a consistent fit of the hyperfine splitting in both the high- and low-field sets of lines, the hyperfine parameters had to be varied such that $A=a\bar{A}$ and $A'=b\bar{A}$ (a and b are the same values used to fit the Zeeman parameters P and Q). This is taken as evidence that the Γ_8 state is relatively well isolated and the Zeeman and hyperfine interactions sample the same angular momentum distributions. Based on these P, Q, and $\bar{A}$ values, spectra were then calculated for $\vec{H}\parallel(111)$ and $\vec{H}\parallel(112)$. In addition, three of the $\Delta I_z=\pm1$ forbidden lines for $\vec{H}\parallel(101)$ and $\vec{H}\parallel(112)$ were calculated for the Pr^{2+} system. The derived parameters for the two systems are given in Table III, and a summary of the differences between experimental and calculated resonance fields is given in Table IV. The last column of Table IV is the error involved in taking the experimental data from the published reports, and is not necessarily the uncertainty in the original experimental data. It is evident that both systems are fit to better than "experimental" error. We shall now consider some details of the fit for the two systems.

The Pr^{2+}/CaF_2 fit is indeed a good one. Several aspects of these data merit notice. The main point under consideration at present is the angular dependence with $\vec{H}$ in the (111) plane. $\vec{H}\parallel(101)$ and $\vec{H}\parallel(112)$ are two orientations of the $\vec{H}$ in this plane. [Actually, $\vec{H}\parallel(101)$ and $\vec{H}\parallel(112)$ are both perpendicular to $(-1,-1,1)$, but the cubic symmetry makes this distinction superfluous.] Behavior of the EPR spectrum for $\vec{H}\perp(111)$ is expected to vary with a period of $\frac{1}{6}\pi$. Angular behavior for $\vec{H}$ in the (111) plane of the calculated Pr^{2+}/CaF_2 spectrum is seen to be a direct consequence of the Γ_8 spin Hamiltonian itself, and does not require any added terms such as distortion in the crystal field (Table IV). The nuclear hyperfine value obtained affords an opportunity to estimate the value of $\langle r^{-3}\rangle$ for Pr^{2+}. The magnetic hyperfine constant is given by

$$\bar{A}=\frac{2\mu_B\mu_N\mu}{I}\langle r^{-3}\rangle\langle J||N||J\rangle ,$$

in which μ_B and μ_N are the Bohr magneton and the nuclear magneton, μ and I are the magnetic moment and nuclear spin, and $\langle J||N||J\rangle$ are given by Abragam and Bleaney.[7] Using $I=\frac{5}{2}$, $\mu=4.16$ nuclear magnetons,[13] and $\langle J||N||J\rangle=0.7822$, $\langle r^{-3}\rangle=4.87a_0^{-3}$ (a_0 is the radius of the first Bohr orbit). Although no published value for $\langle r^{-3}\rangle$ for Pr^{2+} was found in the literature, the value obtained is certainly in agree-

TABLE III. Parameters of the Γ_8 spin Hamiltonian for the systems Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6 (Ref. a). [See Eq. (5).]

	Λ[b]	a	b	P	Q	$\bar{A}$ (MHz)	A(MHz)	A'(MHz)
Pr^{2+}/CaF_2	0.7272	−1.228 (−0.999)[c]	1.190 (1.113)[c]	2.175 (2.258)[c]	−0.465 (−0.360)[c]	1013	−1245	1206
Np^{4+}/Cs_2ZrCl_6	0.744	−0.516 (0.078)[c,d]	0.882 (0.654)[c,d]	2.203 (2.325)[c,d]	−0.148 (0.121)[c,d]	1361	−703	1201

[a] Angular dependence of the observed lines yields relative signs of the a and b parameters. Through Eq. (3), the relative signs of P and Q are therefore determined. Through Eq. (15) the relative sign of A and A' are also determined. The absolute signs of a and b are not obtainable from the observed lines $[(M_s=+\frac{1}{2}\rightarrow M_s=-\frac{1}{2})$ and $(M_s=+\frac{3}{2}\rightarrow M_s=-\frac{3}{2})]$; neither can the relative sign of a and $\bar{A}$ be found from the observed lines. Should other transitions be found it would perhaps be possible to determine the relative signs of a and $\bar{A}$.

[b] Landé g factor. For Pr^{2+}/CaF_2 the value $\Lambda=\frac{8}{11}$ for the $^4I_{9/2}$ state is used. For Np^{4+}/Cs_2ZrCl_6 the value is a value obtained by the mixture of other L states into the ground state for the free ion Np^{4+}. (See Refs. 10 and 27.)

[c] Values in parentheses are the Zeeman parameters reported in Refs. 9 and 10. The large discrepancy between our parameter values and those of Refs. 9 and 10 arise because of their incomplete analysis of the published data. These references derived parameters from spectra based on the assumption that hyperfine structure could be averaged to give an effective electronic Zeeman energy level as might be expected for $I=0$ isotopes. Due to extensive and large off-diagonal terms in the exact Hamiltonian matrix, hyperfine interactions cause both shifts and splittings of the various transitions. Of course numerical diagonalization of the complete Hamiltonian presented here takes these effects into account.

[d] These values are calculated from those in Ref. 10 using Eq. (6b) and redefining P and Q such that $|P|>|Q|$.

ment with trends in the rare-earth series for triply and doubly charged ions.[14,15] Assuming $\langle r^{-3}\rangle_{HF}\sim\langle r^{-3}\rangle_{\text{QUAD}}$ and taking a value of $Q=-0.054$ b for Pr, it is estimated that the effect of quadrupole interaction on forbidden transitions is of the order of 1 G. Therefore, unless the Sternheimer shielding factor is unusually large, the effect of quadrupole interaction on the EPR spectrum should be minimal. This assertion is supported by the fact that the experimental $\Delta I_z=\pm1$ transitions that have been calculated are fit as well as the allowed lines. A definitive answer to the importance of the quadrupole interaction in Pr^{2+}/CaF_2 must await more accurate experimental data, however.

The parameters derived for the Np^{4+} system must be viewed as less accurate than those for the Pr^{2+}

TABLE IV. Average errors (experimental versus calculated) in the systems Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6.

		$H\parallel(001)$	$H\parallel(101)$	$H\parallel(112)$	$H\parallel(111)$	All orientations	Error in published experimental value[b]
Pr^{2+}/CaF_2	Number of transitions in fit	6	15	15	12	48	
	Average fit error (Gauss)	18.1	39.2	71.1	41.0	47.0	±60
Np^{4+}/Cs_2ZrCl_6	Number of transitions in fit	6	12	6[a]	5	29	
	Average fit error (Gauss)	53	103	95[a]	101	91	±130

[a] Only low-field features are included. See text, Sec. IV, for high-field features and discussion.

[b] Taken from published graphs in Refs. 9 and 10. See text for explanation.

system. First, the accuracy to which we could measure data from published tables and graphs was worse (±30 vs ±60 G). Second, there seems to be a problem with the data for $\vec{H}\perp(111)$. Note that in Fig. 3 of Ref. 10, there is asymmetry of the observed resonance frequencies about $\theta=0°$. Cubic symmetry requires resonance fields to be the same for $\theta=-30°$ $[\vec{H}\parallel(1\,-2\,1)]$ and $\theta=+30°$ $[\vec{H}\parallel(2\,-1\,-1)]$. This is obviously not the case for the experimental data, as there are differences of 300 to 400 G between these two orientations. Note that the resonance fields for $\theta=-60°$, $0°$, and $+60°$ are in agreement. These observations seem to indicate either a slight misorientation of the crystal or a distortion of the crystal symmetry. Calculations for $\vec{H}\parallel(112)$ give an average error of 95 G for the six low-field lines, but the six high-field lines are calculated low by an average value of 740 G. This latter deviation is based on an average of the experimental lines for $\theta=+30°$ and $\theta=-30°$. Note, however, in Table IV, that for 23 lines calculated with $\vec{H}$ in three other orientations, the average error is only 90 G (less than the measurement error). The five lines calculated for $\vec{H}\parallel(111)$ are all high-field lines. As a result, we feel the discrepancy between measured and calculated results in the high-field lines for $H\parallel(112)$ is probably due to an internal inconsistency in the experimental data set. Our calculation does, however, show the dramatic angular dependence for the $\vec{H}\perp(111)$ plane. For example, the highest field line is calculated at 20 990 G for $H\parallel(101)$ and at 22 776 G for $H\parallel(112)$. So the Np^{4+} system again confirms that angular dependence in the $\vec{H}\perp(111)$ plane is due mainly to the Γ_8 Hamiltonian itself, and not to other interactions. Finally, we wish to emphasize that the Γ_8 spin-Hamiltonian parameters reported in Table III for Np^{4+}/Cs_2ZrCl_6 are probably accurate only to within about ±5%. A more accurate determination of the parameters must await a more extensive and self-consistent data set.

B. Crystal-field parameters

Zeeman interaction parameters in these two systems may be used to estimate the relative importance of the fourth- and sixth-order contributions to the cubic crystal field as measured by the parameter χ, defined by Lea, Leask, and Wolf.[16] ($\chi=\pm1.0$ implies a pure fourth-order crystal field, whereas $\chi=0$ implies a pure sixth-order crystal field.) Using the wave functions of Lea *et al.*, P and Q were calculated as a function of χ. The experimental values of P and Q were then compared with the theoretical P and Q values to give a resultant χ value. These calculations assume a free ion Landé g factor Λ. Results of this procedure are reported in Table V, in the rows headed by $k=1.0$ (k is a reduction factor such $\Lambda_{\text{eff}}=k\Lambda$).

TABLE V. Ratios of fourth- and sixth-order terms in the cubic crystal field as derived from the Zeeman parameters for Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6.

	Fit No.	Reduction factor k	$\Lambda_{\text{eff}}=k\Lambda$	$\chi(P)$	Derived[a]	$\chi(Q)$
Pr^{2+}/CaF_2	Pr	1.000	0.727	−0.518		−0.542
		0.936	0.681		−0.542	
Np^{4+}/Cs_2ZrCl_6	Np1	1.000	0.744	−0.520		−0.561
		0.921	0.685		−0.561	
	Np2	1.000	0.744	. . .[b]		+0.515
		0.746	0.555		+0.475	
	Np3	1.000	0.744	. . .[b]		+0.732
		0.753	0.560		+0.764	

[a] $\chi(P)$ and $\chi(Q)$ are the values of χ derived from the experimental values of P and Q, respectively, using the listed value of $k\Lambda$. χ is defined by the relation $B_4/B_6=[\chi/(1-|\chi|)][F(4)/F(6)]$ where B_4 and B_6 are, respectively, the fourth- and sixth-order crystal field constants. $F(4)$ and $F(6)$ are constants. See Ref. 16 for further discussion. Uncertainty in χ is 0.005.

[b] For the free-ion value of the Landé g factor, $\Lambda=0.744$, the experimental value of P does not give a graphical solution for positive χ.

P and Q should give the same χ value but it is obvious from Table V that this is not the case for the free-ion Landé g factor. By letting k vary from 1.0 to $\chi(P)$ and $\chi(Q)$ values are brought into agreement for all cases in Table V.

In CaF_2 the Pr^{2+} ion is at the body center of a cube of eight F^- ions, and a point-charge crystal-field model predicts a negative χ value for this system, in agreement with the value obtained. Np^{4+} is at the center of an octahedron of Cl^- ions in Cs_2ZrCl_6 and the χ value is predicted to be positive by a point-charge crystal-field model.

Table V shows that in the case of Np^{4+}/Cs_2ZrCl_6, fits are obtained for both positive and negative values of χ. The two positive χ fits require much larger reductions from the free-ion Landé g factor than does the negative χ fit. Raubenheimer *et al.*[17] report values for crystal-field parameters in Pa^{4+}/Cs_2ZrCl_6 that give a value of $\chi=0.503$. Satten *et al.*[18] report crystal-field parameters in U^{4+}/Cs_2ZrCl_6 that yield a value $\chi=0.434$. The radial parameters $\langle r^4\rangle$ and $\langle r^6\rangle$ given by Lewis *et al.*[19] may be employed to predict χ values for Np^{4+} from those of Pa^{4+} and U^{4+}. Since $\chi=0.535$ and $\chi=0.453$ obtain for Pa^{4+} and U^{4+} respectively, the value $\chi=0.475$ for Np^{4+} seems more reasonable with respect to other Cs_2ZrCl_6 values than does the $\chi=0.764$ value. Based on the present EPR data for the Np^{4+}/Cs_2ZrCl_6 system alone, however, it is not clear that χ should be positive.

Explanation of these reduction factors is a matter of some interest and difficulty, several mechanisms having been proposed. Mixing of other J levels of the lowest free-ion term into the ground state (e.g., ${}^4I_{11/2}$ into ${}^4I_{9/2}$) would require $k>1.0$. Covalency, that is mixing of the ligand ion orbitals with those of the central ion, is often formulated in just this manner in terms of reduction factors. Indeed, one would expect more covalency in the case of Cl^- ligands than in the case of F^- ligands, just as the experimental data seem to indicate.

Another possible explanation for the discrepancy between experimental and theoretical g values is mixing of various crystal-field states into the ground state by the ion lattice interaction.[20–23] This mechanism has been successful in rationalizing such discrepancies in several rare-earth systems in recent years.[24,25] Both systems in question most likely have Γ_6 and Γ_8 excited states within a few hundred wave numbers of the ground state[16,26,27]; mixing of these states into the ground Γ_8 by the ion-lattice interaction could account for the observed parameters.

Thus, both covalency and ion-lattice interaction can be seen to account for the discrepancy in the P and Q derived crystal-field ratios. Interpretation of the reduction factor k, if this is indeed the proper way to achieve consistency between theoretical and experimental spin-Hamiltonian parameters, must await further theoretical and experimental analysis.

IV. CONCLUSIONS

We have shown that angular dependence in the EPR spectrum of $\Gamma_8(O_h)$ states, as observed in Pr^{2+}/CaF_2 and Np^{4+}/Cs_2ZrCl_6 systems, is a consequence of the Γ_8 Hamiltonian itself and not some neglected interaction or distortion in the crystal symmetry. In cases for which hyperfine interactions are large, fitting the experimental data is not a straightforward process, but requires a sizeable amount of calculation, depending, of course, on the value of the nuclear spin. Lastly, important data on crystal-field interactions (ratios between various orders of the crystal-field expansion) may be obtained from an analysis of the spin-Hamiltonian parameters.

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