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ANALYSIS OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM
OF DIVALENT Es IN CaF₂*

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Abstract

An analysis of the spin Hamiltonian parameters of divalent Es (Es III) in cubic sites in CaF₂ has shown that for this ion 1) the ratio of crystalline field parameters $-B_6/B_4 < 0.21$; the orbital reduction factor $(1-k) = 0.033 \pm 0.005$; and the value of the nuclear moment of ²⁵³Es is $\mu_N = (+) 3.62 \pm 0.5$ nm.

I. INTRODUCTION

Dipositive lanthanide ions (Xe core, $4f^n$) stabilized in the alkaline earth fluorides have been intensively studied by optical and magnetic resonance techniques.¹⁻⁴ Comparisons with atomic beam data on the corresponding free atom ground states (Xe core, $4f^n, 6s^2$), which have similar electronic properties but no crystalline field effects, have proved fruitful. From the lowering of the Landé g value (g_J) in the dipositive ion with respect to the free atom, covalency has been determined;⁵⁻⁷ and from differences in the hyperfine structure constants, core polarization effects have been found.^{7,8} Dipositive Am^9 (Ra core, $5f^7$) has until recently¹⁰ been the only dipositive actinide ion stabilized in alkaline earth fluorides. The analyses of the hyperfine structure of this ion and of Pu IV (spectroscopic notation) have shown much larger core polarization effects for the $5f$ series than for the $4f$ series.¹¹ Dipositive Es (Ra core, $5f^{11}$) has been stabilized in CaF_2 and identified by its electron paramagnetic resonance spectrum.¹⁰ Although atomic beam data are not yet available for Es I (Ra core, $5f^{11}, 7s^2$) a reasonable estimate of g_J from extrapolated parameters can be made. An analysis of the spin-Hamiltonian parameters of dipositive Es is described in this paper; a limit is placed on the ratio of the crystalline field parameters, the importance of covalent bonding is estimated by use of the orbital reduction factor, and a value for the nuclear moment of ^{253}Es ($I = 7/2$)¹² is obtained.

The electron paramagnetic resonance spectrum at 4.2°K consisted of eight isotropic lines which were fitted to the spin Hamiltonian

$$\mathcal{H} = g \beta \bar{H} \cdot \bar{S}' + A \bar{I} \cdot \bar{S}' \quad , \quad (1)$$

with $S' = 1/2$ and $I = 7/2$. The values of the parameters are listed in Table I. The agreement between the measured g value with that calculated for a Γ_6 state of a pure $^4I_{15/2}$ multiplet ($g_{\text{calc.}} = -6.0$) in cubic symmetry was close enough to enable this spectrum to be assigned to dipositive $^{253}\text{Es.}^{10}$

II. THEORY AND RESULTS

A. Ratio of Crystalline Field Parameters

The electronic configuration of Es III outside closed shells is $5f^{11}$. The ground term is mainly 4I which, including the effects of spin orbit coupling, will have a $J = 15/2$ multiplet lowest. The spin orbit interaction mixes states with different L and S but is diagonal in J so this quantum number may be used to label intermediate coupled states in the absence of J mixing by the crystalline field. The crystalline field Hamiltonian for cubic symmetry is written as

$$\begin{aligned} \mathcal{H} = & B_4 [c_0^{(4)} + (\frac{5}{14})^{1/2} (c_{-4}^{(4)} + c_4^{(4)})] \\ & + B_6 [c_0^{(6)} - (\frac{7}{2})^{1/2} (c_{-4}^{(6)} + c_4^{(6)})] \quad , \end{aligned} \quad (2)$$

where

$$c_q^{(k)} = \left[\frac{4\pi}{(2k+1)} \right]^{1/2} Y_{kq} \quad ,$$

and the Y_{kq} are normalized spherical harmonics.¹³ This potential will split the sixteen fold degenerate $J = 15/2$ state into two doublets, Γ_6 and Γ_7 , and 3 quartet Γ_8 states. The relative energies of these five crystalline field states depend only on the ratio of the crystalline field parameters, B_4 and B_6 . By determining which crystalline field state has the lowest energy we may set a limit on the ratio B_6/B_4 . Graphs of the crystalline field energy levels vs a parameter related to the ratio of B_6/B_4 have been given for cubic symmetry by Lea, Leask, and Wolf¹⁴ for all J states between 2 and 8 in half integral steps. A similar graph has been

given specifically for the f^{11} system in eightfold coordination by Weakliem and Kiss,² (Fig. 7 in their paper) and since our convention for the crystalline field Hamiltonian is the same as these authors, we have used their graph to determine $-B_6/B_4 < 0.21$ for the Γ_6 state to be lowest.¹⁵ If the ratio $-B_6/B_4 > 0.21$, the Γ_7 state would be lowest which is contrary to the experimental result. This result for Es III in CaF_2 is the same as that found for Ho III in the alkaline earth fluorides.^{1,2}

B. Covalent Effects

In the absence of crystalline field mixing of J levels the measured g value for the Γ_6 state of Es III should equal

$$g = -5 g_J \quad , \quad (3)$$

where g_J is the Lande g value for the free ion Es III. In order to determine g_J for Es III in intermediate coupling we have used extrapolated values for the Slater radial parameter F_2 and the spin orbit coupling constant ξ and assumed hydrogenic ratios for F_4/F_2 and F_6/F_2 to determine these other Slater radial parameters.¹³ The electrostatic and spin orbit matrix was diagonalized and the resultant ground state eigenvector was used to calculate an intermediate coupled g_J value. The parameters F_2 and ξ were reasonably varied¹⁶ and it was found that g_J was not sensitive to these parameters. The results are summarized in Table II. Experimentally (Eq. (3)) we find $g_J = 1.162 \pm 0.002$.

In order to determine the effect of crystalline field mixing on the measured g value, the electrostatic, spin-orbit and crystalline field matrix elements for the f^{11} configuration were calculated and the resulting matrix diagonalized. A truncated basis set was used which is shown in Table III.

The L-S basis set and the J states needed were chosen from the most important terms determined in the first calculation. Only the J = 9/2 through 15/2 states were included in the diagonalization. This matrix was checked by comparing our eigenvalues for Ho III with those given by Weakliem and Kiss.² There was excellent agreement for this lanthanide ion. A value of F_2 and ξ were taken from the previous calculation of electrostatic and spin orbit matrix elements, and the crystalline field parameters obtained for Pu IV were used.¹⁷ Dirac Slater calculations¹⁸ show $\langle r^4 \rangle_{\text{Pu IV}} > \langle r^4 \rangle_{\text{Es III}}$ and $\langle r^6 \rangle_{\text{Pu IV}} > \langle r^6 \rangle_{\text{Es III}}$ so the Pu IV crystalline field parameters are a reasonable approximation for dipositive Es. The results of these calculations are shown in Table IV. The value of g_J found from this calculation is 1.185. The mechanism of crystalline field mixing of J levels therefore might account for approximately 10% of the reduction of g_J .

It has been shown from fluorine ENDOR experiments on rare earth ions⁵ and Pu IV¹⁹ that covalent bonding is present in rare earth and actinide ions doped in alkaline earth fluorides. We now assume covalent bonding is the most important mechanism causing the reduced g_J value although we can not rule out the orbit-lattice interaction described by Inoue.²⁰

The effect of covalent bonding will be to reduce the orbital angular momentum. This effect is parameterized by the introduction of the orbital reduction factor. Following Bleaney⁷

$$g_{J_{\text{Es III}}} - g_{J_{\text{exp}}} = \delta g_J = -(2 - g_J)(1 - k) \quad , \quad (4)$$

where (1-k) is the reduction in the orbital k-factor. For Es III, (1-k) = 0.033 ± 0.005 ; the uncertainty includes the possibility of the J mixing contributing to the g_J reduction. Table V lists values of (1-k) for various ions in CaF_2 .

C. Hyperfine Structure

The non-relativistic hyperfine Hamiltonian is

$$\mathcal{H} = \frac{2\beta\beta_N\mu_N}{I} \sum_i \frac{\mathbf{N} \cdot \mathbf{I}}{r_i^3} + \frac{8\pi}{3} \sum_i \delta(\mathbf{r}_i) \mathbf{s}_i \cdot \mathbf{I} \quad (5)$$

where β and β_N are the Bohr and nuclear magneton respectively, μ_N is the nuclear moment, I the nuclear spin, \mathbf{r}_i the radius vector for the i th electron, and $\delta(\mathbf{r}_i)$ is the Dirac delta function which is non-zero only for s electrons. The operator \mathbf{N}_i is written in tensor operator notation as

$$\mathbf{N}_i = \mathbf{l}_i - (10)^{1/2} (\mathbf{s}_i \mathbf{C}^2)_i^{(1)} \quad (6)$$

where \mathbf{l}_i and \mathbf{s}_i are the orbital and spin angular momentum vectors and $\mathbf{C}^{(2)}$ is a second rank tensor.²¹ We have used this Hamiltonian and typical wavefunctions obtained from the parameters discussed previously and calculated the matrix elements needed to derive a nuclear moment from the measured hyperfine constant. In these calculations we have assumed that no J mixing by the crystalline field occurs. The two largest uncertainties in this calculation are the value of $\langle 1/r^3 \rangle_{\text{Es III}}$ and the magnitude of the term which transforms as the operator \mathbf{s}_i which includes both f electron relativistic effects and core polarization effects.^{22,23} If we now make the assumption that the magnetic field per unit spin at the nucleus is constant throughout the actinide series,⁷ we may calculate core polarization and relativistic f electron effects in Es III from our previous result on Pu IV,¹¹

$$a_c = - (556 \pm 42) (g_J - 1) \frac{\mu_N}{I} \text{ Mc/sec} \quad (7)$$

This assumption was made by Bleaney for the lanthanide series,⁷ but experimental evidence on Tm III²⁴ and theoretical calculations by Freeman and Watson²⁵ have questioned the validity of it. Although this assumption is probably incorrect we have used it in order to estimate the magnitude of core polarization for Es III.

Table VI lists the values of the matrix elements needed. We have converted our measured hyperfine coupling constant for the Γ_6 state to its free ion value by

$$|a| = \frac{|A|}{-5} \quad , \quad (8)$$

where a is the hyperfine coupling constant for the free ion. The hyperfine coupling constant may be broken up into two terms

$$a_{\text{exp}} = a_f + a_c \quad , \quad a_f = 4 \beta \beta_N \frac{\mu_N}{I} \langle 1/r^3 \rangle [\langle \psi | \mathcal{N}_1 | \psi \rangle] \quad , \quad (9)$$

where a_f comes from the first part of Eq. (5) and a_c , the core polarization term (including relativistic effects) comes from the second part of Eq. (5). In order to evaluate a_f we need values of $\langle 1/r^3 \rangle$ for Es²⁺. Recent relativistic calculations of Lewis et al.¹⁸ have tabulated values of $\langle 1/r^3 \rangle$ and these are reproduced in Table VII for Es I and Es III. Since these calculations are relativistic $\langle 1/r^3 \rangle_\ell \neq \langle 1/r^3 \rangle_{\text{SC}}$ ² as is true in the non relativistic Hamiltonian and $\langle 1/r^3 \rangle_s$ gives the relativistic correction for f electrons but does not include core polarizations effects. In previous work it was found that $\langle 1/r^3 \rangle_\ell$ given by Dirac Slater calculations was low by approximately 9% but $\langle 1/r^3 \rangle_s$ agreed with experimental measurements for free atoms.¹¹ In Table VIII we tabulate values of the

nuclear moment of ^{253}Es calculated using various approximations 1) $\langle 1/r^3 \rangle_\ell$ as given by Dirac Slater calculations and a_c as given by Eq. (7), 2) $\langle 1/r^3 \rangle_\ell$ given by Dirac Slater calculations and a_c including only relativistic effects as given by the Dirac Slater calculations; 3) $\langle 1/r^3 \rangle_\ell$ increased by 9% as found previously, a_c given by Eq. (7); 4) $\langle 1/r^3 \rangle_\ell$ increased by 9%, a_c including only relativistic effects as given by the Dirac Slater calculations. In these calculations we have assumed $\langle 1/r^3 \rangle_\ell = \langle 1/r^3 \rangle_{SC}^2$ because as shown previously¹¹ when the angular factors are considered this approximation will affect the results by less than 1%. Also $\mu_N^{253\text{Es}}$ and therefore a_{exp} have been assumed to be positive since nuclear systematics²⁶ and Schmidt diagrams²⁷ predict this sign.

III. DISCUSSION

If we assume the lowering of the g value is due to covalent bonding then we can compare the value found for Es III with the lanthanide series. Table V gives this comparison which shows more covalency for the actinide ion than for the lanthanide ions. This effect is not surprising since the more extended 5f orbitals result in greater overlap with ligand orbitals than do the 4f orbitals. The ratio of the crystalline field parameters is again as found in Ho III, the corresponding lanthanide. This result agrees with our previous conclusion that actinide ions with $Z > 94$ in alkaline earth fluoride lattices will have properties similar to those found in the lanthanide series.¹⁷ It will be of interest to compare the hyperfine coupling constants of Es I and Es III (this work) when atomic beam data on the free atom become available. The quantities $\langle 1/r^3 \rangle$ for Es I and Es III (from Table VII) differ by less than 1%. The dipole part a_f depends almost entirely on the matrix element containing the operator $\tilde{\ell}_i$ which according to the g

value analysis is reduced by about 3% for Es III as compared with Es I. Again according to Table VII, the relativistic effects for 5f electrons are approximately the same for Es I and Es III. Previous work^{11,18} has shown that core polarization effects in the hyperfine structure of free atoms of the actinide series are small or negligible so any difference in the hyperfine structure constant of $a_{\text{Es I}} - a_{\text{Es III}}$ greater than $\sim +4\%$ may be assigned to core polarization of the ion.

In our calculation of the nuclear moment of ^{253}Es the main error is the value of $\langle 1/r^3 \rangle_{\ell}$. Our previous work on Pu IV showed the Dirac Slater calculation to be low. We estimated the magnitude of core polarization to be -3.5% . We now arbitrarily correct the value of $\langle 1/r^3 \rangle_{\ell}$ by $+5\%$ and give as the value of $\mu_{\text{N}}(^{253}\text{Es}) = (+) 3.62 \pm 0.5 \text{ nm}$. Our value of the nuclear moment is considerably lower than the one derived from the analysis of the emission spectra of Es II;¹² ($|\mu_{\text{N}}| = 5.1 \pm 25\% \text{ nm}$) but somewhat larger than the value obtained from nuclear orientation experiments²⁶ ($|\mu_{\text{N}}| = 2.7 \pm 1.3 \text{ nm}$).

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FOOTNOTES AND REFERENCES

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Table I. Spin Hamiltonian Parameters for $^{253}\text{Es III}$ (Ref. 10)

$$|g| = 5.809 \pm 0.005$$

$$|A| = (0.1216 \pm 0.002)\text{cm}^{-1}$$

Table II. Parameters used to calculate free ion g values

F_2	ξ	g_J
308	3226	1.191
308	3649	1.189
308	3913	1.188
320	3226	1.190
320	3649	1.188
320	3913	1.187
358	3226	1.189
358	3649	1.188
358	3913	1.187
358	4220	1.188
Mean		1.189 ± 0.002

Table III. Basis set used for the calculation of electrostatic, spin-orbit, and crystalline field matrix elements. (Notation from C. W. Nielson and G. F. Koster, "Spectroscopic Coefficients for the p^n , d^n , f^n Configuration," Technology Press, Cambridge, Massachusetts, 1963)

4_F	2_{G_1}
4_G	2_{G_2}
4_I	2_{H_1}
	2_{H_2}
	2_I
	2_K
	2_L

Table IV. Effect of crystalline field mixing on the g value of the Γ_6 state

Ion	ξ (cm^{-1})	F_2 (cm^{-1})	B_4 (cm^{-1})	B_6 (cm^{-1})	g_{Γ_6}
Ho^{2+}	1980	395	2360	-465	5.974
Es^{2+}	4220	358	6200	-1240	5.924
Es^{2+}	4220	358	0	0	1.188

Table V. Orbital reduction factors for various ions in CaF_2

Ion	Configuration	(1-k)	Reference
Ho^{2+}	$4f^{11}$	0.016 ± 0.001	7
Tm^{2+}	$4f^{13}$	0.009 ± 0.001	7
Yb^{3+}	$4f^{13}$	0.016 ± 0.001	5
Er^{2+}	$5f^{11}$	0.033 ± 0.005	(this work)

Table VI. Numerical values for the hyperfine matrix elements with varying parameters

Parameters		Operators				
F_2 (cm^{-1})	ξ (cm^{-1})	\tilde{l}_i	$-10^{1/2}(\tilde{s} \tilde{c}^2)_i^{(1)}$	\tilde{N}_i	\tilde{s}_i	$2(\tilde{l}_i + 2\tilde{s}_i)$
337	3226	0.8098	-0.0354	0.7744	0.1902	1.190
358	4220	0.8127	-0.0378	0.7750	0.1873	1.187
308	3913	0.8139	-0.0386	0.7753	0.1861	1.186

Table VII. Results of Dirac-Slater calculations for
Es I and Es III (from Ref. 18)

	$\langle 1/r^3 \rangle_{l_i}$	$\langle 1/r^3 \rangle_{(sc^2)_i}^1$	$\langle 1/r^3 \rangle_{s_i}$
Es I	10.19	12.57	-1.10
Es III	10.27	12.55	-1.05

Table VIII. Calculated values for the magnetic dipole moment μ_N of ^{253}Es .
 (See text for the explanation of differences between the calculations)

Calculation	$a_f \left(\frac{I}{\mu_N}\right) \text{Mc/sec}$	$a_c \left(\frac{I}{\mu_N}\right) \text{Mc/sec}$	$\mu_N (\text{nm})$
1	(+) 772.9	-104.0	(+) 3.81
2	(+) 772.9	- 79.0	(+) 3.68
3	(+) 842.2	-104.0	(+) 3.46
4	(+) 842.2	- 79.0	(+) 3.34

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