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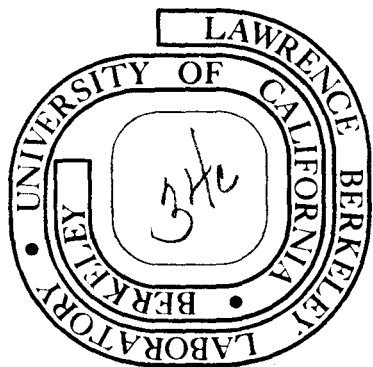
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THE EPR OF Cf^{3+} IN OCTAHEDRAL SYMMETRY AND
THE NUCLEAR DIPOLE MOMENT OF $^{249}\text{Cf}^*$

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ABSTRACT

The epr spectrum of the ground Γ_6 state of ^{249}Cf has been measured. The derived spin Hamiltonian parameters are $g = 6.273 \pm 0.010$ and $A = (7.52 \pm 0.2) \times 10^{-3} \text{ cm}^{-1}$. The nuclear spin $I=9/2$ has been confirmed and a value $|\mu| = .28 \pm .06 \mu_N$ for the nuclear dipole moment has been calculated from the hyperfine coupling constant.

The diamagnetic compounds $\text{Cs}_2\text{NaMCl}_6$ ($M = \text{Y}^{3+}$ or Lu^{3+}) provide an excellent lattice for magnetic and optical investigations of the trivalent $4f^n$ and $5f^n$ ions.^{1,2} The octahedral coordination about the f^n ion $(\text{MCl}_6)^{3-}$ particularly simplifies the analysis of the experimental results.³ We report in this paper the electron paramagnetic resonance (epr) spectrum of $^{249}\text{Cf}^{3+}$ diluted in $\text{Cs}_2\text{NaLuCl}_6$. The spin Hamiltonian parameters of Yb^{3+} present in our sample as an additional impurity are also given. From an analysis of the spin Hamiltonian parameters of Cf^{3+} the value of the nuclear magnetic dipole moment of ^{249}Cf is determined. This work is the first report of the magnetic properties of Cf^{3+} in a well defined symmetry site.

EXPERIMENTAL PROCEDURES AND RESULTS

Approximately 1 mg ^{249}Cf generated by β -decay of the 314-day ^{249}Bk was purified from other metal ions first by pressurized ion exchange chromatography with *Dowex* 50W-X8 cation exchange resin in a 10-cm-long x 1-cm-ID column and then by a second chromatographic separation on a 5-cm-long x 2-mm-ID column.⁷ Both columns were eluted with ammonium α -hydroxybutyrate solution at $\sim 80^\circ\text{C}$. The purified ^{249}Cf was adsorbed from the ammonium α -hydroxybutyrate solution on *Dowex* 50W-X8 cation resin. The column was washed with 1M HCl and eluted with 6M HCl.

$\text{Cs}_2\text{NaLuCl}_6$, doped with ^{249}Cf , was prepared by adding stoichiometric amounts of CsCl, NaCl, and $\text{LuCl}_6 \cdot \text{XH}_2\text{O}$ to 6M HCl, adding a 6M HCl solution of ^{249}Cf , evaporating to a solid, drying this material in quartz to 400°C , and then fusing by lowering in a sealed quartz tube at 2 mm/hr through a 950°C

vertical furnace. The product was a polycrystalline material; the sample used for epr measurements contained approximately .5wt% ^{249}Cf . The epr spectra were measured at 4.2°K and at a frequency of approximately 35GHz with the equipment previously described.⁴

The epr spectrum of the polycrystalline Cf^{3+} in $\text{Cs}_2\text{NaLuCl}_6$ sample is shown in Figure 1. The ten hyperfine lines confirm the nuclear spin I of ^{249}Cf as 9/2. The measured parameters of the applicable spin Hamiltonian

$$H = g \mu_B \vec{H} \cdot \vec{S}' + A \vec{I} \cdot \vec{S}' \quad (1)$$

where the effective spin $S' = 1/2$ and $I = 9/2$, are given in Table 1. The only other strong lines in the sample appeared at high magnetic fields and were assigned to Yb^{3+} from the measured g value (Table 1) and the characteristic hyperfine patterns. For the Yb^{3+} ion the effective spin is $S' = 1/2$ and $I = 0$ for the even-even isotopes which are 69.56% abundant, $I = 1/2$ for ^{171}Yb (14.31% abundant), $I = 5/2$ for ^{173}Yb (16.31% abundant).

DISCUSSION

Let us consider an isolated J level for an f transition ion in O_h symmetry. The energy levels and eigenvectors then depend only on the ratio and sign of the sixth order crystal field term to the fourth order term.³ Lea, Leask, and Wolf³ have tabulated these eigenvalues and eigenvectors for all J manifolds of the f^n series ($n=1-13$) and predicted the crystal field ground states for the rare earth ions in cubic and octahedral symmetry. We may use this formulation of the problem for actinide ions; however we have to calculate the effects of intermediate coupling on the fourth and sixth order operator equivalent factors, β and γ , and on the free ion Lande'

g value, g_J . These parameters are shown in Table 2. We have used the electrostatic and spin orbit parameter values obtained by Carnall et al⁵ to calculate these numbers. We did not use their configuration interaction parameters which will not greatly affect the ground state wavefunction. As can be seen from Table 2 the signs of the operator equivalent factors are not changed by the inclusion of intermediate coupling effects. Therefore the ground crystal field state should be either a Γ_6 or Γ_7 doublet which will which will give an isotropic epr spectrum.

The calculated g value for the Γ_6 state, $-5g_J$, is equal to -6.395 for Cf^{3+} . The calculated g value for the Γ_7 state is $5.667g_J$. Therefore we assign the epr spectrum to the Γ_6 state which allows us to set a limit on the ratio of the sixth to the fourth order crystal field parameter $B_6^0/B_4^0 < 1.32$.^{6,7,8} This ratio is consistent with the limits found by Hendricks et al.¹

HYPERFINE STRUCTURE AND THE NUCLEAR DIPOLE MOMENT

If we use the relationship

$$\frac{A}{g} = \frac{a}{g_J}$$

we find the free ion hyperfine coupling constant

$$|a| = 1.50 \pm .04 \text{ MHz.}$$

The nuclear dipole moment is related to the free ion hyperfine coupling constant by⁹

$$a = \frac{2\mu_B \mu_N \mu}{I} \langle \frac{1}{r} \rangle \langle LSJ || N_i || LSJ \rangle ,$$

where μ_B and μ are the Bohr and nuclear magneton respectively, μ is the nuclear dipole moment, and $\langle \frac{1}{r} \rangle$ the expectation value of the radial wave function.

We have assumed the core polarization term is negligible. The operator \vec{N}_i is defined.^{8,9}

$$\vec{N}_i = \sum_i [\vec{l}_i - 10^{\frac{1}{2}} (\vec{s}C^2)_i^{(1)}]$$

where \vec{l}_i and \vec{s}_i are the spin and orbital angular momentum vectors and $C^{(2)}$ is a second rank tensor. We calculate

$$|\mu| (^{249}\text{Cf}) = .28 \pm .06 \mu_N$$

where we have corrected the \vec{l}_i part of the tabulated N matrix element for the effects of intermediate coupling. The value of $\langle \frac{1}{r^3} \rangle$ was obtained from Lewis et al.¹⁰ The error is estimated from uncertainties in the parameters used.

The ^{249}Cf nuclear ground state has been assigned to 9/2-[734] Nilsson level.¹¹ The formalism for calculating nuclear dipole moments for single neutron states from Nilsson wave functions is well known.¹² If we use for effective g values¹³ $g_s^{\text{eff}} = -2.4$, $g_e^{\text{eff}} = -0.03$, $g_R = 3.5$, and a deformation parameter $\eta=4$ we find

$$\mu (^{249}\text{Cf}) = -0.49 \mu_N$$

The absolute value calculated for nuclear moment depends to some degree on the deformation parameter chosen. The agreement between the experimental and the theoretical result is fair.

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7. We are using the tensor operator notation given by Wybourne (Reference 9). The crystal field potential for O_h symmetry is

$$V_c = B_0^4 [C_0^{(4)} + (5/14)^{\frac{1}{2}} (C_{-4}^{(4)} + C_4^{(4)})] + B_0^6 [C_0^{(6)} - (7/2)^{\frac{1}{2}} (C_{-4}^{(6)} + C_4^{(6)})]; C_q^{(k)} = \left[\frac{4\pi}{(2k+1)} \right]^{\frac{1}{2}} Y_q^{(k)},$$
 the $Y_q^{(k)}$ and normalized spherical harmonics.
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Table 1. Spin Hamiltonian parameters of $^{249}\text{Cf}^{3+}$ and various Yb^{3+} isotopes diluted in $\text{Cs}_2\text{NaLuCl}_6$.

Ion	I	g	$\left \frac{A}{g\mu_B} \right $ (gauss)	A ($\text{cm}^{-1} \times 10^3$)
$^{249}\text{Cf}^{3+}$	9/2	6.273 ± 0.010	25.7 ± 0.7	7.52 ± 0.2
Yb^{3+}	0	2.586 ± 0.004		
Yb^{3+} ^a	0	2.584 ± 0.002		
$^{173}\text{Yb}^{3+}$ ^a	5/2	2.584 ± 0.002	157.4 ± 0.5	$18.99 \pm .06$
$^{171}\text{Yb}^{3+}$ ^a	1/2	2.584 ± 0.002	577.4 ± 1	$69.66 \pm .12$

^aFrom unpublished measurements at 4.2°K at a frequency of $\sim 9.2\text{GHz}$.

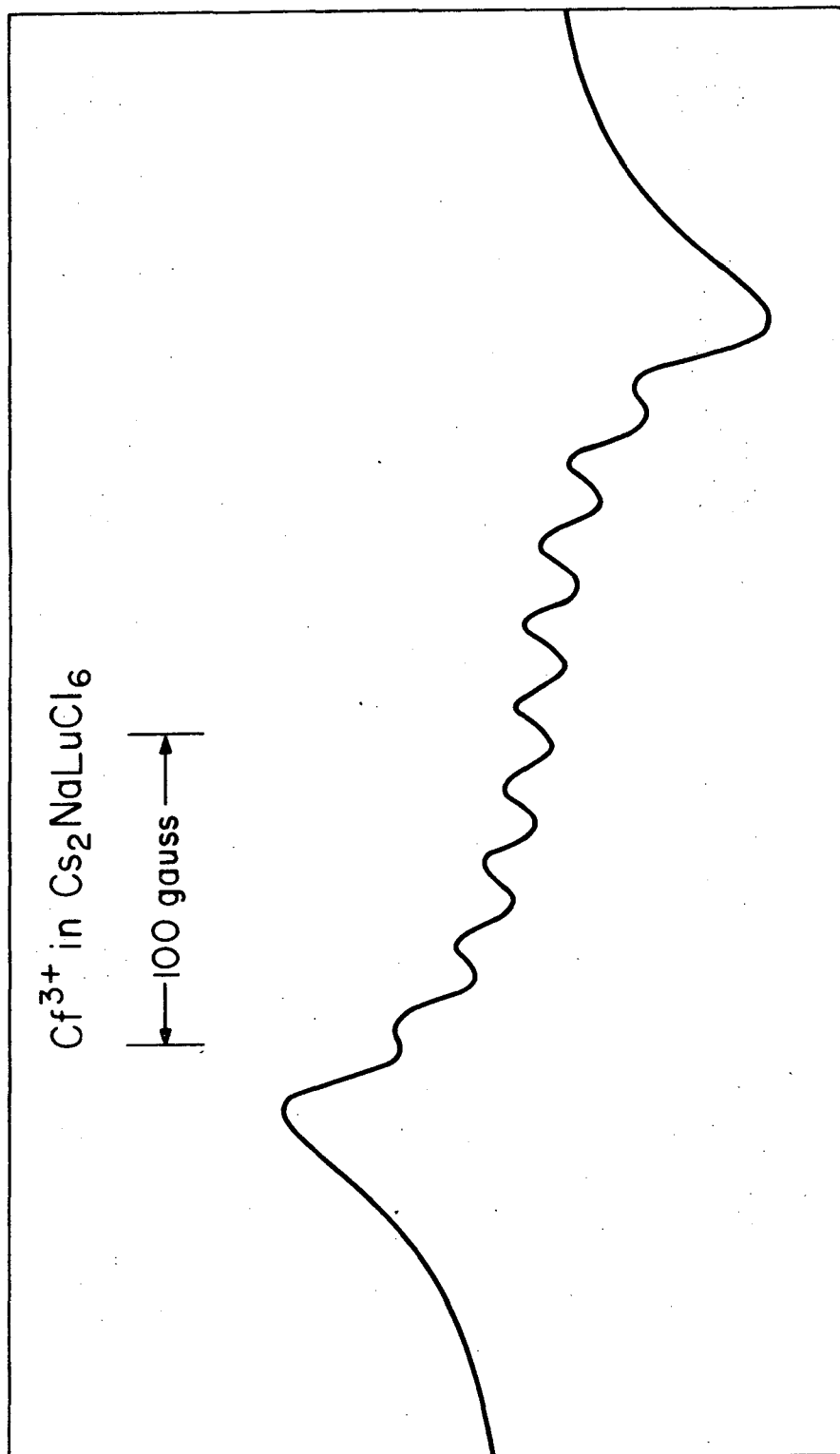
Table 2. Operator equivalent factors and free ion g values for the ground state of the f^9 ions.

Ion	$\beta \times 10^4$	$\gamma \times 10^6$	g
$4f^9 \text{ Dy}^{3+}$ a	-0.5920	1.0350	1.333
$5f^9 \text{ Cf}^{3+}$	-0.5602	.4494	1.279

From Reference 3.

FIGURE CAPTIONS

Fig. 1. EPR spectrum of Cf^{3+} in $\text{Cs}_2\text{NaLuCl}_6$, $T = 4.2^\circ\text{K}$, the frequency is approximately 35GHz.



XBL 744-2905

Fig. 1

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