

Electron Paramagnetic Resonance Investigations of Divalent Americium and Trivalent Curium in Strontium Chloride*

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The cubic-site electron-paramagnetic-resonance spectra of divalent americium and trivalent curium ($5f^7$ configuration) in SrCl_2 have been observed. The ground states are Γ_6 doublets, indicating that the fourth-order parameters c of the cubic crystal-field Hamiltonian are negative. Because of the relatively small cubic crystal-field interaction with the ${}^8S_{7/2}$ state, the Γ_6 ground-state transitions were anisotropic, permitting a determination of $\frac{1}{4}$ the zero-field splitting. Additionally, an excited state (Γ_7) resonance was detected for curium, and curium resonances were observed at temperatures as high as 200 K. The g_J value obtained for Cm^{3+} was 1.9264 ± 0.0008 while the Am^{2+} g_J value was 1.9283 ± 0.0008 . Assuming that the sixth-order parameters are negligible, the values of c are $-1.83 \pm 0.02 \text{ cm}^{-1}$ for curium and $-1.92 \pm 0.16 \text{ cm}^{-1}$ for americium. The hyperfine structure constants for americium were determined to be $83.9 \pm 0.1 \text{ G}$ for ${}^{241}\text{Am}$ ($I = \frac{5}{2}$) and $8.32 \pm 0.1 \text{ G}$ for ${}^{243}\text{Am}$ ($I = \frac{7}{2}$). The previously unknown nuclear spin of ${}^{245}\text{Cm}$ was determined to be $\frac{7}{2}$ with an A value of $19.0 \pm 0.2 \text{ G}$. By comparison with ${}^{241}\text{Am}$ and ${}^{243}\text{Am}$, an estimate of the magnetic moment $|\mu({}^{245}\text{Cm})| = (0.5 \pm 0.1)\mu_N$ was made.

INTRODUCTION

ALTHOUGH numerous electron-paramagnetic-resonance (EPR) investigations of ground-state splittings of the $4f^7$ configuration ions Eu^{2+} and Gd^{3+} have been carried out, relatively little information exists concerning similar properties of the $5f^7$ analog ions Am^{2+} and Cm^{3+} . Electron resonance spectra of Cm^{3+} have previously been observed in the fluorite-structure hosts ThO_2 ,¹ CeO_2 ,¹ and CaF_2 ,^{2,3} as well as in the hexagonal hosts LaCl_3 ⁴ and $\text{La}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.⁴ The EPR spectrum of Am^{2+} has been reported only in CaF_2 .^{2,3} Since both $4f^7$ and $5f^7$ configuration ions have a Hund's-rule ${}^8S_{7/2}$ ground state, one would expect to observe similar behavior when the ions are incorporated into isomorphous host crystals. The investigations noted above, however, have pointed out the following important distinctions in the properties of ions belonging to these two configurations. Ground-state splittings reported to date for $5f^7$ configuration ions have been considerably larger than those of isovalent $4f^7$ ions in identical host crystals. Observed departures of the Landé g factor g_J from the free-electron value are much larger for $5f^7$ than for $4f^7$ ions. Finally, due to a relatively shorter spin-lattice relaxation time, the spectra of $5f^7$ ions reported previously could only be observed at liquid-hydrogen temperature or below, in contrast to the usual situation for the $4f$ analogs (exceptional $4f^7$

cases being Tb^{4+} in ThO_2 ,⁵ and CeO_2 ,⁶ and Eu^{2+} in ThO_2 .⁷) These differences imply that the $5f^7$ ground state contains significant admixtures of non- S -state levels. Edelstein and Easley³ have argued that the differences might be explained by using intermediate coupled wave functions which would arise as a result of the large actinide spin-orbit coupling interaction. They indicated that this intermediate-coupling approach does at least lead to an ordering of the states that agrees with experiment.

Although the exact nature of the interaction between an S state and the crystalline electric field is not fully understood, symmetry considerations show that a cubic crystal field reduces the degeneracy of an ${}^8S_{7/2}$ state to a Γ_6 doublet, a Γ_8 quartet, and a Γ_7 doublet (listed in order of increasing energy, consistent with a negative fourth-order parameter c). Considering the three cases in which Cm^{3+} has previously been studied in a cubic site,^{1,2} it is interesting to note that the crystalline electric field splitting in each instance was so large that only one isotropic transition, arising from an isolated Γ_6 ground doublet, was observed at a frequency of approximately 10 GHz. For Cm^{3+} in CaF_2 ³ (as well as Am^{2+}) this transition was anisotropic at a frequency of 35 GHz, since the increased magnetic field admixed the higher Γ_8 quartet. Measurements of this anisotropy enabled Edelstein and Easley³ to make the first calculation of the $\Gamma_8 \rightarrow \Gamma_6$ separation for a $5f^7$ ion. Strontium chloride was chosen as the host crystal in this investigation because its lattice constant is considerably larger than that of CaF_2 and therefore could be expected to result in significantly reduced crystalline electric field splittings. Trivalent gadolinium has a smaller splitting

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¹ M. M. Abraham, C. B. Finch, and G. W. Clark, *Phys. Rev.* **168**, 933 (1968).

² N. Edelstein, W. Easley, and R. McLaughlin, *J. Chem. Phys.* **44**, 3130 (1966).

³ N. Edelstein and W. Easley, *J. Chem. Phys.* **48**, 2110 (1968).

⁴ M. M. Abraham, B. R. Judd, and H. H. Wickman, *Phys. Rev.* **130**, 611 (1963).

⁵ J. M. Baker, J. R. Chadwick, G. Garton, and J. P. Hurrell, *Proc. Roy. Soc. (London)* **A286**, 352 (1965).

⁶ Yu. S. Greznev, M. M. Zaripov, and V. G. Stepanov, *Fiz. Tverd. Tela* **7**, 3644 (1965) [*Soviet Phys. Solid State* **7**, 2937 (1966)].

⁷ M. M. Abraham, C. B. Finch, R. W. Reynolds, and H. Zeldes, *Phys. Rev.* **187**, 451 (1969).

in SrCl_2 ⁸ than in any of the other fluorite structures,⁹ and it was anticipated the situation would be similar for Cm^{3+} . The resulting reduction in the separation of the levels and the associated increase in spin-lattice relaxation time could make it possible to observe transitions between higher-lying levels. An excited-state resonance was, in fact, observed; the transition due to the ground Γ_6 doublet was anisotropic even at 9 GHz. The $\Gamma_8 \rightarrow \Gamma_6$ separation for both Cm^{3+} and Am^{2+} could thus be determined for purposes of comparison with the results for Cm^{3+} and Am^{2+} in CaF_2 .³ The resonance associated with the excited Γ_7 level was observed only at temperatures above 4.2 K and is the first reported observation for a $5f^7$ ion of a transition other than that due to the ground-state doublet. Trivalent curium resonances were observed at temperatures up to 200 K.

Hyperfine structure was observed for $^{241}\text{Am}^{2+}$ and $^{243}\text{Am}^{2+}$ in SrCl_2 ; and by utilizing isotopically enriched Cm, the nuclear spin of the odd isotope ^{245}Cm ($T_{1/2} = 8265 \pm 180$ yr)¹⁰ was observed to be $\frac{7}{2}$. This represents the first direct measurement of the ^{245}Cm nuclear spin.

THEORY

The cubic-field spin Hamiltonian¹¹

$$3C = g_J \beta \mathbf{H} \cdot \mathbf{J} + B_4 [O_4^0 + 5O_4^4] + B_6 [O_6^0 - 21O_6^4], \quad (1)$$

where $J = S = \frac{7}{2}$, can be used to describe the splitting of the $^8S_{7/2}$ ground state of Am^{2+} and Cm^{3+} . Introducing the customary fourth- and sixth-order parameters $c = 4b_4^0 = 240B_4$ and $d = 4b_6^0 = 5040B_6$ and choosing the Γ_7 doublet at zero energy, the eigenvalues of Eq. (1) at zero applied magnetic field are

$$\begin{aligned} \Gamma_7: \quad E &= 0, \\ \Gamma_8: \quad E &= 20b_4^0 + 28b_6^0 = 5c + 7d, \\ \Gamma_6: \quad E &= 32b_4^0 - 8b_6^0 = 8c - 2d. \end{aligned} \quad (2)$$

Exact expressions for the eigenvalues in the presence of a magnetic field applied along the $[100]$ axis have been given elsewhere.¹² For this magnetic field direction and for a crystal-field splitting significantly greater than the microwave energy, the g values (assuming an effective spin $S' = \frac{1}{2}$ for the transitions within the Γ_6 and Γ_7

doublets) are given by the expressions^{1,13}

$$g_{\Gamma_6} \approx \frac{1}{3}(7g_J) \left[1 + \frac{20(g_J \beta H)^2}{[3c - 9d]^2} \right], \quad (3)$$

$$g_{\Gamma_7} \approx 3g_J \left[1 - \frac{4(g_J \beta H)^2}{[5c + 7d]^2} \right]. \quad (4)$$

For magnetic field directions other than $\mathbf{H} \parallel [100]$, the second term in each bracket of Eqs. (3) and (4) will be different, indicating the admixture of the Γ_8 with the Γ_6 and Γ_7 lines. For very large values of c relative to the applied microwave energy, this admixture is not significant, and the resonance transitions within the Γ_6 and Γ_7 doublets are isotropic with g values $g_{\Gamma_6} = (7/3)g_J$ and $g_{\Gamma_7} = 3g_J$. For smaller c , appreciable admixing with the Γ_8 will occur, resulting in anisotropy in the Γ_6 and Γ_7 resonance transitions.

EXPERIMENT

A. Crystal Growth

Single crystals of SrCl_2 (melting point 875°C) were grown in evacuated quartz ampoules using the vertical Bridgman technique. The water-cooled thermal gradient furnace used for crystal growth was enclosed by a glove box which afforded protection from the predominantly α -radiation hazard. Transuranic dopants were prepared as anhydrous trichlorides by evaporating to dryness (at $\sim 40^\circ\text{C}$) aqueous solutions of 1 mole transuranic oxide and 3 moles NH_4Cl in an excess of HCl . This leaves a relatively anhydrous, nonhygroscopic solid solution of the transuranic trichloride in NH_4Cl .¹⁴ The resulting residue, after storage for several days in a desiccator, was introduced into a conical-bottomed 0.6-cm-i.d., 20-cm-long quartz tube. The NH_4Cl was sublimed off the dopant residue by simultaneously heating (~ 400 – 500°C) and evacuating. This procedure prevented the formation of transuranic oxychlorides. After the system was returned to room temperature and atmospheric pressure, that portion of the tube containing the NH_4Cl was removed. Approximately 5 g of pure SrCl_2 crystal fragments were then quickly added. The use of previously purified single crystals eliminated the difficulties associated with the presence of waters of hydration. The tube was again evacuated and heated at $\sim 400^\circ\text{C}$ for 30 min prior to sealing with an oxypropane torch. The resulting ampoule was then lowered through a thermal gradient of approximately $20^\circ\text{C}/\text{cm}$ (at 875°C) at a rate of 0.25 cm/h.

At the end of a typical run, the quartz was frequently cracked owing to adhesion of the solidified crystal,

⁸ M. M. Abraham and L. A. Boatner, *J. Chem. Phys.* **51**, 3134 (1969).

⁹ M. M. Abraham, L. A. Boatner, and E. J. Lee, *Phys. Letters* **25A**, 230 (1967).

¹⁰ D. N. Metta, H. Diamond, and R. F. Kelly, *J. Inorg. Nucl. Chem.* **31**, 1245 (1969).

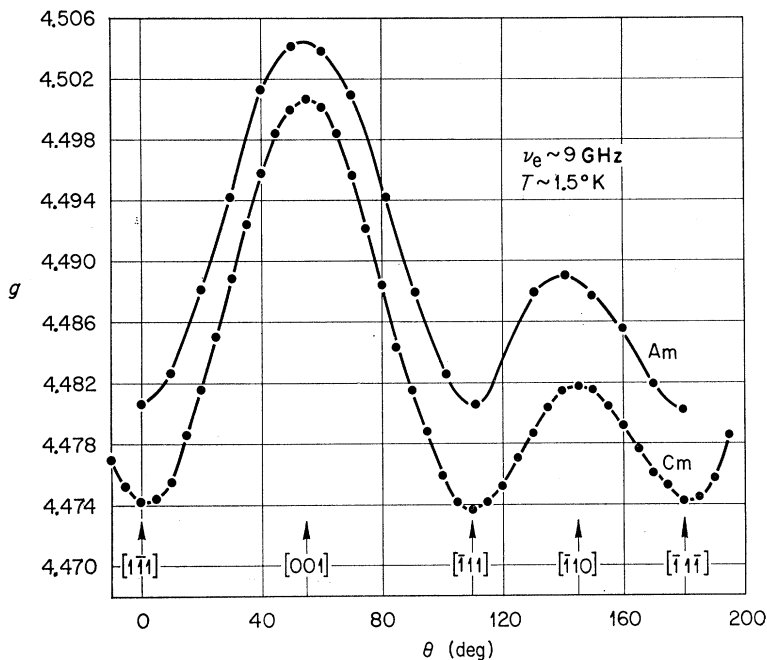
¹¹ K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids* **23**, 1381 (1962).

¹² For example, M. M. Abraham, L. A. Boatner, C. B. Finch, E. J. Lee, and R. A. Weeks, *J. Phys. Chem. Solids* **28**, 81 (1967) and references therein.

¹³ P. P. Pashinin and A. M. Prokhorov, in *Paramagnetic Resonance*, edited by W. Low (Academic, New York, 1963), Vol. 1, p. 197.

¹⁴ L. B. Asprey, *Inorg. Chem.* **3**, 1137 (1964).

FIG. 1. Angular variation in the (110) plane of the Γ_6 ground-state g value for Cm^{3+} and Am^{2+} in SrCl_2 .



which contracted on cooling. However, this usually had a minimal effect on the crystals, which were up to $3 \times 4 \times 6$ mm in size. The crystals were broken out of the ampoule and, being hygroscopic, were stored in a desiccator. Before removal from the glove box, the crystals were coated with an acrylic spray (Krylon) to prevent absorption of water vapor and to attenuate the α emission. (Crystals which are not sprayed will cause contamination.)

The curium-doped crystals were initially light blue in color, but rapidly darkened as a result of the intense internal α bombardment. (The crystals could be bleached by a thermal anneal at $\sim 500^\circ\text{C}$.) At room temperature, they emitted a vivid blue phosphorescence. Upon warming from 77 K to room temperature, at least three separate thermoluminescence glow peaks (two red and one green) were observed. The intense radioactivity (principally due to the ^{244}Cm) also reduced the initially trivalent Am to the desired divalent state as well as producing the Cl_2^- center which has been observed previously in SrCl_2 .¹⁵ Crystals doped only with americium were yellow in color and exhibited no room-temperature phosphorescence.

The SrCl_2 single crystals were doped with a total transuranic concentration of approximately one to two parts in 500 (by weight). The first crystal growth run showed spectra due to ^{244}Cm , ^{245}Cm , ^{241}Am , and ^{243}Am . Later runs were made with ^{241}Am alone and with isotopically enriched Cm ($\sim 23.5\%$ ^{245}Cm , 65.7% ^{244}Cm , 10.6% ^{246}Cm , 0.1% ^{247}Cm , and 0.1% ^{248}Cm).

¹⁵ H. Bill, H. Suter, and R. Lacroix, Phys. Letters 22, 241 (1966).

B. Resonance Results

The EPR spectra were observed at a frequency of 9 GHz on a conventional homodyne spectrometer using a back-diode detector. The strontium chloride single crystals were mounted with a $[110]$ axis vertical in a TE_{011} -mode cylindrical cavity. By rotating the applied magnetic field in the (110) plane, the resonance spectrum could be investigated along each of the three principal crystallographic directions.

For the Γ_6 state of $^{244}\text{Cm}^{3+}$ in a cubic site, the g value should be $(7/3)g_J$, as noted above. The g_J value for Cm^{3+} would be expected to be close to that found for Cm^{3+} in CaF_2 ($g_J = 1.926$), resulting in a value of $(7/3)g_J$ equal to 4.494. At 4.2 K, an intense, slightly anisotropic line was observed which had the following extrema in the (110) plane: $g_{100} = 4.501 \pm 0.002$, $g_{111} = 4.473 \pm 0.002$, $g_{110} = 4.482 \pm 0.002$, and was thus identified as the Cm^{3+} Γ_6 cubic-site resonance. The anisotropy in the g value indicates that the crystal-field interaction is small enough that magnetic-field-induced admixtures of the nearby Γ_8 level are appreciable. The line width also varied slightly with magnetic field orientation, the narrowest width being 3 G with $\mathbf{H} \parallel [111]$ and the broadest being 5 G with $\mathbf{H} \parallel [100]$.

Approximately centered about the ^{244}Cm resonance were two similar spectra due to ^{241}Am ($I = \frac{5}{2}$) and ^{243}Am ($I = \frac{5}{2}$). These spectra consisted of two sets of six hyperfine lines with an isotropic (in magnetic field) hyperfine splitting and an anisotropic g value. The g values for the Am^{2+} spectra are $g_{100} = 4.504 \pm 0.003$, $g_{111} = 4.481 \pm 0.003$, and $g_{110} = 4.489 \pm 0.003$. The Am^{2+}

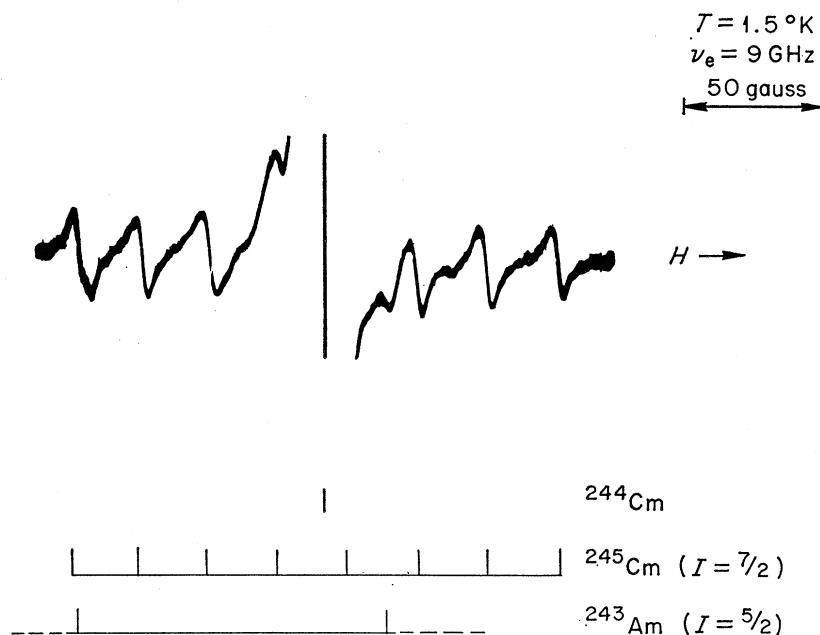


FIG. 2. EPR Spectrum of Cm^{3+} and Am^{2+} in SrCl_2 showing ^{245}Cm hyperfine structure and two of the six ^{243}Am hyperfine lines.

linewidths were also anisotropic and exhibited a variation similar to that described above for Cm^{3+} . Figure 1 shows the experimentally determined angular variations of the Cm and Am g values. Also centered on the $^{244}\text{Cm}^{3+}$ resonance was a weak eight-line hyperfine pattern which was attributed to ^{245}Cm . Resonance observations of crystals doped with isotopically enriched ^{245}Cm confirmed this conclusion and established the ^{245}Cm nuclear spin to be $\frac{7}{2}$. Figure 2 shows the ^{245}Cm resonance observed in the enriched crystal. The hyperfine constants are given in Table I.

In addition to the cubic-site spectra described above, axially symmetric spectra were observed whose line width varied with magnetic field orientation, thus making measurements impractical. No hyperfine structure was observed in these spectra. (However, the axial sites were not studied in the ^{245}Cm -enriched crystals.) A Cm^{3+} spectrum with $\langle 111 \rangle$ symmetry was definitely observed, and resonances were seen which were thought to arise from Cm^{3+} in a site with $\langle 100 \rangle$ symmetry. A tentative assignment of $g_{11} = 7.45$ and $g_1 = 3.02$ was made for the $\langle 100 \rangle$ symmetry site, although all three equivalent sites were not observed. The average g value of 4.50 indicates that the distortion produces a small perturbation of the ^{244}Cm Γ_6 ground state. At least two isotropic lines of unknown origin were also observed with g values of 7.00 ± 0.01 and 1.120 ± 0.001 . The widths of these lines varied with magnetic field orientation. The magnetic field region around $g = 2$ contained numerous intense resonance lines due to Cl_2^- centers¹⁵ which were produced by α radiation in the crystal. This Cl_2^- spectrum was useful in orienting the crystal.

At 10 K, the ^{244}Cm Γ_6 resonance was observed with a linewidth of 12 G. At this temperature, an additional

resonance was detected which was isotropic within experimental error at $g = 5.782 \pm 0.006$ with a linewidth of 20 G. This line is attributed to the Cm^{3+} excited Γ_7 state whose g value is expected to be $3g_J = 5.778$. Relative intensities at 10 K of this line and the Γ_6 resonance are consistent with this explanation. The expected Γ_7 anisotropy should be smaller than the Γ_6 since $|E_{\Gamma_7} - E_{\Gamma_8}| > |E_{\Gamma_8} - E_{\Gamma_6}|$. The strongest resonance associated with the Γ_8 level, which is lower in energy than the Γ_7 , was obscured by the Cl_2^- spectrum, which spans the region in which this Γ_8 resonance should occur. Both the Γ_6 and Γ_7 lines could be observed at elevated temperatures with linewidths exceeding 100 G. The Γ_6 resonance was detected below 200 K, and the Γ_7 below 180 K. The Am^{2+} resonances were not observed at 77 K probably as a result of reduced signal strength owing to a lower concentration of americium in the crystals and the distribution of intensities among the hyperfine transitions.

DISCUSSION

The resonances observed previously at 9–10 GHz for Cm^{3+} in cubic hosts^{1,2} are examples of the situation in which the crystal-field splitting is quite large relative to the microwave energy, and no anisotropy is seen in the Γ_6 ground states. For the cases of Cm^{3+} and Am^{2+} in SrCl_2 treated here, the condition $|3c - 9d|^2 \gg 20(g_J\beta H)^2$ in Eq. (3) was not fulfilled at 9 GHz, and the Γ_6 transitions were anisotropic. Measurements of these anisotropies were used to determine the $\Gamma_8 \rightarrow \Gamma_6$ splittings and g_J values. This determination was accomplished by a computer program which carried out an exact diagonalization of the matrix of Eq. (1) for the states of $J = \frac{7}{2}$. The $\Gamma_8 \rightarrow \Gamma_6$ splittings (denoted by ΔE) for

TABLE I. Spin-Hamiltonian parameters and zero-field splittings of Am^{2+} and Cm^{3+} in CaF_2 and SrCl_2 .

Crystal	T (K)	g_J	ΔE (cm^{-1})	$c^a = \Delta E/3$ (cm^{-1})	A (G)	Reference
			Cm^{3+}			
CaF_2	4.2	1.9261 ± 0.001	13.4 ± 0.5	-4.5 ± 0.2		^b
SrCl_2	4.2	1.9264 ± 0.0008	5.48 ± 0.06	-1.83 ± 0.02	${}^{245}A = 19.0 \pm 0.2$	^c
			Am^{2+}			
CaF_2	4.2	1.9258 ± 0.001	18.6 ± 0.5	-6.2 ± 0.2	${}^{241}A = 87.64 \pm 0.05$ ${}^{243}A = 86.89 \pm 0.05$	
					$\frac{{}^{241}A}{{}^{243}A} = 1.009 \pm 0.001$	^b
SrCl_2	4.2	1.9283 ± 0.0008	5.77 ± 0.48	-1.92 ± 0.16	${}^{241}A = 83.9 \pm 0.1$ ${}^{243}A = 83.2 \pm 0.1$	
					$\frac{{}^{241}A}{{}^{243}A} = 1.008 \pm 0.001$	^c

^a ΔE is the energy difference between the Γ_6 and Γ_8 levels; the fourth-order parameter c is calculated from ΔE by assuming d , the sixth-order parameter, is zero.

^b N. Edelstein, W. Easley, and R. McLaughlin, *J. Chem. Phys.* **44**, 3130 (1966); N. Edelstein and W. Easley, *ibid.* **48**, 2110 (1968).

^c This work.

Cm^{3+} and Am^{2+} resulting from this procedure are listed in Table I, along with the corresponding g_J values. The parameters obtained³ at 35 GHz for Cm^{3+} and Am^{2+} in CaF_2 are given for purposes of comparison. Also tabulated are the fourth-order parameters c , which have been calculated assuming that the sixth-order crystal-field terms are negligibly small.

Since the Γ_7 resonance was observed, it is possible, in principle, to calculate the $\Gamma_7 \rightarrow \Gamma_8$ splitting from the anisotropy of the Γ_7 level. Knowing both the $\Gamma_7 \rightarrow \Gamma_8$ and $\Gamma_8 \rightarrow \Gamma_6$ splittings, one could then calculate c and d . Anisotropy of the Γ_7 line would, of course, be expected to be considerably less than that of the Γ_6 since the splitting between the Γ_7 and Γ_8 levels for $\mathbf{H} \parallel [100]$ exceeds that between the Γ_6 and Γ_8 levels by $|2c + 16d|$. Unfortunately, the anisotropy of the Γ_7 resonance proved to be so small (lying within experimental error) that the $\Gamma_7 \rightarrow \Gamma_8$ separation could not be found by this method. A measurement of the $\Gamma_7 \rightarrow \Gamma_6$ separation for Cm^{3+} was achieved, however, by observing relative intensities of the two transitions at 10 K. The $\Gamma_7 \rightarrow \Gamma_6$ separation ($8c - 2d$) determined by this method was $23 \pm 8 \text{ cm}^{-1}$. The $\Gamma_7 \rightarrow \Gamma_6$ separation calculated from the more accurately measured value of the $\Gamma_8 \rightarrow \Gamma_6$ splitting by assuming $d = 0$ is $14.6 \pm 0.2 \text{ cm}^{-1}$. Although the uncertainty associated with the relative-intensity technique is high, the discrepancy between these values implies that d may not be zero, that it may have the same sign as c (i.e., negative), and could, in fact, be as high as 10–15% of the c value. A significant d value for a $5f^7$ ion in a fluorite-structure host would contrast with that of every $4f^7$ ion observed previously in this type structure.^{12,16} The d values found for the $4f^7$ ions in monoxide hosts with an NaCl-type structure are, of course, appreciable^{12,16} (a value of d which is 50% of c

¹⁶ L. A. Boatner and M. M. Abraham (unpublished).

has been reported¹⁷), but the signs of c and d are opposite in these hosts.

The results of the present investigation serve to point out some basic similarities between EPR spectra of $4f^7$ and $5f^7$ configuration ions. From Table I, it is apparent that the crystal-field splittings of Cm^{3+} and Am^{2+} are larger in CaF_2 than in SrCl_2 , which is analogous to the behavior of Gd^{3+} and Eu^{2+} in these hosts.^{9,12,18} Additionally, the difference between the Am^{2+} and Cm^{3+} splitting is larger³ in CaF_2 than in the inflated SrCl_2 lattice, which is identical to the behavior observed for the Eu^{2+} and Gd^{3+} impurities. (The Eu^{2+} and Gd^{3+} splittings are almost identical^{9,18} in SrCl_2 while the Eu^{2+} splitting in CaF_2 is about 21% larger than that of Gd^{3+} in the same host.¹²)

From the results of Edelstein and Easley³ we calculate the ratio of the experimentally determined fourth-order parameters of Cm^{3+} and Gd^{3+} in CaF_2 to be

$$\text{CaF}_2: b_4(\text{Cm}^{3+})/b_4(\text{Gd}^{3+}) = 232. \quad (5)$$

The b_4 value for Gd^{3+} in CaF_2 at 4.2 K¹⁹ was used in determining this ratio, which differs from the value of 243 given by Edelstein and Easley,³ who apparently used the room-temperature $\text{CaF}_2:\text{Gd}^{3+}$ b_4 value.¹² The corresponding ratio for Cm^{3+} and Gd^{3+} in SrCl_2 is given by

$$\text{SrCl}_2: b_4(\text{Cm}^{3+})/b_4(\text{Gd}^{3+}) = 276. \quad (6)$$

¹⁷ K. E. Mann and L. V. Holroyd, *Phys. Status Solidi* **28**, K27 (1968).

¹⁸ R. W. Reynolds, L. A. Boatner and M. M. Abraham (to be published).

¹⁹ M. M. Abraham, L. A. Boatner, E. J. Lee, and R. A. Weeks, in Proceedings of the Sixth Rare Earth Research Conference, Gatlinburg, Tenn., p. 89, 1967 (unpublished).

For Am^{2+} and Eu^{2+} the b_4 ratios are given by the terms

$$\begin{aligned} \text{CaF}_2: b_4(\text{Am}^{2+})/b_4(\text{Eu}^{2+}) &= 264, \\ \text{SrCl}_2: b_4(\text{Am}^{2+})/b_4(\text{Eu}^{2+}) &= 285, \end{aligned} \quad (7)$$

whose values are close to those for Cm^{3+} and Gd^{3+} . Using intermediate coupled wave functions for both the Cm^{3+} and Gd^{3+} , Edelstein and Easley³ have calculated this ratio $b_4(\text{Cm}^{3+})/b_4(\text{Gd}^{3+})$ to be 511. The qualitative agreement with the experimental values shows that, at least for the fourth-order parameters, the intermediate coupling mechanism can probably account for the difference in the crystal-field splittings between the $4f^7$ and $5f^7$ ions.

It is interesting to note that in SrCl_2 the g_J value for Am^{2+} is greater than that of Cm^{3+} , although in CaF_2 they were approximately equal.³ This g_J difference would be expected,²⁰ since the Cm^{3+} spin-orbit coupling constant is larger than that of Am^{2+} and should therefore result in greater intermediate coupling effects (i.e., a larger departure of g_J from 2). The ratio of the Am hyperfine constant was measured by Fred and Tompkins²¹ using optical spectroscopy to be $^{241}A/^{243}A = 1.008 \pm 0.001$, and by Edelstein and Easley,³ from EPR data, to be 1.009 ± 0.001 . Our result of 1.008 ± 0.001 is in excellent agreement.

The EPR spectra of $3d^5$ and $4f^7$ ions have exhibited hyperfine structure that was initially unexpected but later explained as being due to a combination of configuration interaction²² (i.e., a partial admixture of unpaired s electrons into the ground electronic configurations) and exchange polarization of the core

²⁰ B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).

²¹ M. Fred and F. S. Tompkins, *J. Opt. Soc. Am.* **47**, 1076 (1957).

²² A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 135 (1951).

electrons by the spin of the $3d$ or $4f$ electrons.²³ Relativistic effects,²⁰ which become more important as Z increases, also have to be considered.

Without making any assumption about the mechanism causing S -state hyperfine splitting, one may make an estimate of the magnetic moment of ^{245}Cm from the A value. The product AI is proportional to the magnetic moment μ , and we find that the proportionality constant is not only relatively independent of the host crystal but is practically the same for the $4f^7$ ions, divalent europium and trivalent gadolinium (in spite of the small difference in $\langle 1/r^3 \rangle$ for the two ions). For the analogous $5f^7$ ions, assuming that the different proportionality constant obtained for the three americium isotopes 241, 242, 243 is the same for ^{245}Cm and using the known values for the magnetic moments for the divalent americium isotopes,^{21,24} we may calculate an approximate value for the magnetic moment of the trivalent ^{245}Cm isotope. The result is

$$|\mu(^{245}\text{Cm})| = (0.50 \pm 0.1)\mu_N,$$

where the error reflects the uncertainty in this procedure.

Although nuclear decay schemes²⁵ have implied that the ^{245}Cm nuclear spin is $\frac{7}{2}$, this work represents the first direct measurement of the nuclear spin.

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²³ See, for example, A. J. Freeman and R. E. Watson, *Phys. Rev.* **127**, 2058 (1962), and references cited therein.

²⁴ L. Armstrong, Jr. and R. Marrus, *Phys. Rev.* **144**, 994 (1966); R. Marrus and J. Winocur, *ibid.* **124**, 1904 (1961); R. Marrus, W. A. Nierenberg, and J. Winocur, *ibid.* **120**, 1429 (1960).

²⁵ Y. A. Ellis and A. H. Wapstra, *Nucl. Data Sheets* **B3-2-27** (1969).