rule) over five orders of magnitude. There are difficulties with the interpretation of the observed data which prohibit assignment of the edge to either an indirect or a direct process. The ER data indicate that the observed results of this experiment are not consistent with the Franz-Keldysh effect. It can be more readily explained on the basis of shifts or splitting in the major oscillator due to induced polarization.

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# Electron Spin Resonance of Tripositive Curium in $ThO_2$ and $CeO_2$†

M. M. Abraham, C. B. Finch, and G. W. Clark
*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

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The ESR spectra of $^{244}Cm^{3+}$-doped $ThO_2$ and $CeO_2$ single crystals were measured at approximately 10 Gc/sec and liquid-helium temperatures. Sites of cubic symmetry were observed in both hosts, with the crystal-field splitting being larger than the microwave quanta used. The ground states are $\Gamma_6$ doublets, indicating that the fourth-order parameter of the cubic crystal-field Hamiltonian is negative. For $ThO_2$, the $g$ value was $4.484\pm0.002$, and for $CeO_2$, it was $4.475\pm0.002$.

## INTRODUCTION

The rare-earth elements (also called lanthanide or $4f$ elements) are characterized by the progressive filling of the $4f$ electronic shell. The $f$-electron orbits contract with increasing atomic number (lanthanide contraction) and are shielded by an outer closed shell of $5s$ and $5p$ electrons (with $5d$ and $6s$ valence electrons) from the local chemical environment. This is the reason for the close similarity in the chemical properties of the rare earths.

The possibility of a second rare-earth series beginning at uranium was postulated by Bohr.[1] Following the discovery of synthetic transuranium elements, Seaborg[2] proposed that actinium (element 89) was the analog of lanthanum (element 57) and that the $5f$ electronic shell was being filled. The $5f$ electron eigenfunctions have larger orbits and a lower binding energy than their corresponding $4f$ eigenfunctions; hence, their interaction with the local environment is greater. Further, the actinide contraction (the $5f$ electrons become shielded by an outer closed shell of $6s$ and $6p$ electrons) does not occur as rapidly. This results in a greater variety of valence states for the early actinides with the trivalent state becoming dominant in the later actinides.

When the $4f$ shell is half filled ($Gd^{3+}$ and $Eu^{2+}$) the $^8S_{7/2}$ ground state has no orbital angular momentum and therefore the local crystal field has a smaller effect on the ground-state levels. The spin-lattice relaxation times are long enough for paramagnetic-resonance spectra to be observed at room temperatures for these ions.

The actinide $Cm^{3+}$ nominally has a $5f^7$ configuration and would be expected to exhibit similar resonance spectra. Indeed, early ESR work with $Cm^{3+}$ in lanthanum trichloride and lanthanum magnesium nitrate crystals, unintentionally doped with chemically similar $Gd^{3+}$ as well, erroneously attributed the $Gd^{3+}$ spectra to $Cm^{3+}$.[3] The experiments were performed at room temperature and 77°K only. The $Cm^{3+}$ resonance was first correctly observed in lanthanum trichloride and lanthanum ethylsulfate single crystals at liquid-helium temperatures,[4] and was not observable at 77°K due to the short spin-lattice relaxation time. This, in itself, was a clear indication of a larger crystal-field interaction than usual for $S$-state ions. The observation of only one absorption line instead of the usual seven lines was a further indication of the large interaction with the axial fields in these crystals.

The incorporation of Cm into various host lattices has become desirable and prompted us to incorporate Cm into the cubic fluorite lattices of $ThO_2$ and $CeO_2$.

## EXPERIMENTAL

The $^{244}Cm^{3+}$-doped $CeO_2$ and $ThO_2$ single crystals were grown from $Li_2O\cdot 2WO_3$ flux by a previously described thermal-gradient technique.[5,6] This method

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had allowed substitution of trivalent lanthanide dopant ions for the tetravalent Ce or Th ions, in these hosts with both cubic and axial local symmetries.[7,8] The growth temperatures were 1080–1100°C for the $CeO_2$ and 1275–1300°C for the $ThO_2$.

Since $^{244}Cm$ is a strong $\alpha$ emitter (half-life$=17.6$ years), all crystal growth was carried out in a suitably equipped glove box which provided complete radiation protection. The glove box contained a water-cooled, platinum-wound (16-gauge) resistance furnace having a hot zone 2.0 cm in diameter by 12 cm high. The furnace required a total power input of 500 W to reach 1300°C. The temperatures and thermal gradients in the hot zone could be controlled to $\pm 2$°C by adjusting the current through each of three separate resistance segments. To prevent excessive glove-box flooding in case of leakage, a closed circuit was used for the furnace cooling water.

The $^{244}Cm$ was obtained from the Oak Ridge National Laboratory Isotopes Division as $CmO_2$ powder. The $Li_2O\cdot 2WO_3$, $CeO_2$, and $ThO_2$ were all $>99.99\%$ pure; previous ESR determinations on $CeO_2$ and $ThO_2$ crystals grown with these same reagents had not detected any unintended paramagnetic impurities (except in cases where the growth furnace had been previously contaminated by lanthanides).

In a typical run, 5–7 mg of the $CmO_2$ dopant was mixed with 40 g of 2-mm granules of $Li_2O\cdot 2WO_3$ previously saturated with $CeO_2$ or $ThO_2$ at the prospective growth temperatures. For the case of $ThO_2$, approximately 1–2 wt% $B_2O_3$ was added to the flux to improve growth kinetics. The mixture was melted at 1000°C into a 10-cm-tall, 1-cm-diam (0.5-mm-wall) platinum vessel, having 10–15 g of $CeO_2$ or $ThO_2$ polycrystalline nutrient lumps at its bottom. The vessel was equipped with a thermocouple well, fitted with a platinum foil cover, and inserted into the furnace. The appropriate temperatures and thermal gradients (1080–1100°C, 30°C/6 cm for $CeO_2$; 1275–1300°C, 60°C/6 cm for $ThO_2$) were obtained by providing a predetermined power input to each of the three furnace resistors. The resulting solution level was 6–8 cm from the bottom. Once obtained, the temperatures were maintained constant for two to three weeks. At the end of this period, the vessel and contents were air quenched to room temperature. The resulting octahedral Cm-doped $CeO_2$ or $ThO_2$ crystals generally formed a solid crust across the top liquid surface and prevented decantation of the growth solution at $>1000$°C (which is possible with vessels of larger diameter where complete encrustation does not usually occur). The crystals were broken from the upper container wall and cleaned in concentrated aqueous NaOH at 25–50°C. They were transferred from the glove box to a fume hood and sprayed with transparent acrylic resin. The spraying reduced the $\alpha$ radiation and for further protection the crystals were placed in a 2-mm-i.d. nylon cylindrical capsule.

Both the $CeO_2$ and $ThO_2$ crystals are smaller ($\leq 2$ mm) and of lower quality than those grown by the same technique in larger diameter vessels.[5,6] The Cm-doped $CeO_2$ crystals (Cm:Ce$=1:3000$) are yellow in color. Cm-doped $ThO_2$ crystals (Cm:Th$=1:3000$) are faint rose when first removed from the furnace, but begin to bleach almost immediately at room temperature. The same Cm-doped $ThO_2$ crystals have a red phosphorescence, which is faintly visible in a dark room. No such phosphorescence is apparent in the Cm-doped $CeO_2$. After several weeks the $ThO_2$ crystals turned blue, because of the intense internal $\alpha$ bombardment. Enough time has not elapsed to evaluate whether this also occurs in the $CeO_2$ crystals.

The nylon capsule containing the crystal was mounted on the side wall of a rectangular $TE_{102}$ microwave cavity. The superheterodyne spectrometer (modeled after Hirshon and Fraenkel[9]) operated at $\sim 10$ Gc/sec. No signals were observed at 77°K. At 4.2°K, a single line attributed to $Cm^{3+}$ was observed in both host crystals which was isotropic with respect to magnetic-field orientation. No hyperfine structure was found ($^{244}Cm$ is an even-even isotope and $I=0$). For $ThO_2$, the $g$ value was $4.484\pm 0.002$ and for $CeO_2$, it was $4.475 \pm 0.002$.

By lowering the temperature to $\sim 1.5$°K (pumping on the liquid helium) it was verified that this was a ground-state resonance. The signals could not be saturated at 4.2°K with our superheterodyne spectrometer. The maximum power incident on the cavity was $\sim 1$ mW. However, at 1.5°K, the spin-lattice relaxation time was lengthened enough to allow saturation at a power level of $\sim 10\ \mu$W for both crystals. The blue color in the $ThO_2$ crystals was removed by a 15-min anneal at 800°C, and the crystals were again examined. The relaxation time was longer and saturation was now possible at $\sim 1\ \mu$W and 1.5°K.

The linewidth was approximately 1.5 G in $ThO_2$. In $CeO_2$, the linewidth showed a variation from crystal to crystal which is believed to be due to local strain. The narrowest line observed was $\sim 10$ G in width. When a number of single crystals were put in the cavity at the same time, the lines appeared to be unchanged, verifying the isotropy with respect to crystal orientation in the magnetic field. No axial lines were observed due most probably to the low trivalent ion concentration.[10] An additional isotropic line was observed only in the $ThO_2$ crystals at $g=1.313\pm 0.001$ with the same width as the $Cm^{3+}$ line. Relative intensity measurements between 4.2 and 1.5°K suggested this was not an excited state of $Cm^{3+}$ and the short annealing process greatly attenu-

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[8] M. M. Abraham, R. A. Weeks, G. W. Clark, and C. B. Finch, Phys. Rev. **148**, 350 (1966).

[9] J. M. Hirshon and G. E. Fraenkel, Rev. Sci. Instr. **26**, 35 (1955).

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ated the line intensity relative to the $Cm^{3+}$ line. We hope to explain this line at a later date.

## DISCUSSION

For the Cm-doped ethylsulfate crystals, a single line was observed at helium temperatures characterized by $g_{\parallel}=1.925\pm0.002$ and $g_{\perp}=7.73\pm0.02$.[4] A similar line was observed in the trichloride crystals, the parameters being $g_{\parallel}=1.925\pm0.002$ and $g_{\perp}=7.67\pm0.02$.[4] This was readily explained as the transition between the ground $|\pm\frac{1}{2}\rangle$ doublet whose $g$ values would be

$$g_{\parallel}=2g_J\langle+\tfrac{1}{2}|J_z|+\tfrac{1}{2}\rangle=g_J$$

and

$$\begin{aligned}g_{\perp}=g_J\langle+\tfrac{1}{2}|J_+|-\tfrac{1}{2}\rangle&=g_J[J(J+1)+\tfrac{1}{4}]^{1/2}\\&=g_J[(J+\tfrac{1}{2})^2]^{1/2}=g_J(J+\tfrac{1}{2}).\end{aligned}$$

The axial crystal field splits the eight levels into four doublets and if the splitting is larger than the microwave frequency used, only one transition would be observed. Since this resonance did not disappear on lowering the temperature to 2°K, the $|\pm\frac{1}{2}\rangle$ doublet was the ground doublet. Hence $b_2^0$, the second-order parameter in the axial crystal-field Hamiltonian was positive in both the trichloride and ethylsulfate crystals. This result is analogous to that for $Gd^{3+}$ in the same two crystals.

In a cubic crystal field, the eight levels are split into a $\Gamma_8$ quarter, a $\Gamma_7$ doublet, and a $\Gamma_6$ doublet. At zero field the eigenvalues may be written as[10]

$$\begin{aligned}\Gamma_7&:\ E=0,\\ \Gamma_8&:\ E=5c+7d=\delta,\\ \Gamma_6&:\ E=8c-2d=\delta+\delta',\end{aligned}$$

and with the magnetic field along a [100] direction the energies may be written directly. For $c$ negative, the $\Gamma_6$ doublet is lowest and the energies are

$$E_1=\tfrac{1}{2}(13c+5d+3G)+\tfrac{1}{2}[(3c-9d-\tfrac{2}{3}G)^2+\tfrac{1}{9}(140G^2)]^{1/2},$$

and

$$E_2=\tfrac{1}{2}(13c+5d-3G)+\tfrac{1}{2}[(3c-9d+\tfrac{2}{3}G)^2+\tfrac{1}{9}(140G^2)]^{1/2},$$

where $G=g_J\beta H$. The energy difference is

$$\begin{aligned}E_1-E_2=h\nu=3G+\tfrac{1}{2}[((\delta'-\tfrac{2}{3}G)^2+\tfrac{1}{9}(140G^2))^{1/2}\\-((\delta'+\tfrac{2}{3}G)^2+\tfrac{1}{9}(140G^2))^{1/2}],\end{aligned}$$

so that for $G/\delta'\ll1$,

$$h\nu\simeq\tfrac{1}{3}(7G)+140G^3/27\delta'^2,$$

or

$$g\simeq\tfrac{1}{3}(7g_J)\left[1+\frac{20(g_J\beta H)^2}{9\delta'^2}\right].$$

For $\delta'$ very much larger than the microwave frequency, the $g$ value would be isotropic and approximately equal to $\frac{1}{3}(7g_J)$. At larger magnetic fields (or microwave frequencies), the higher-lying $\Gamma_8$ quartet is admixed with the ground $\Gamma_6$ doublet and there would be an anisotropy in the $g$ value, because the Zeeman interaction of the $\Gamma_8$ quartet is dependent on the field orientation. The variation in the $g$ value would be a reflection of this anisotropic interaction. The maximum $g$ value would occur when $H$ is parallel to a $\langle100\rangle$ axis, while the $g$ value would be a minimum when $H$ is parallel to a $\langle111\rangle$ axis. The amount of anisotropy would be sufficient to determine the $\Gamma_8$-$\Gamma_6$ ground-state splitting. The $Cm^{3+}$ resonance has been observed in $CaF_2$ with an isotropic $g$ value ($g=4.492\pm0.002$) at 10 Gc/sec and showed anisotropy at 35 Gc/sec indicating the $\Gamma_8$-$\Gamma_6$ splitting to be $13.4\pm0.5$ $cm^{-1}$.[11] In the extreme of very large magnetic fields (or small crystal-field splittings) the spectrum would be similar to the usually observed $Gd^{3+}$ spectrum, and all seven lines would be seen.

With the value $g_J=1.925$ taken from the trichloride and ethylsulfate results, $\frac{1}{3}(7g_J)=4.492$. The agreement with the experimental values indicates that the $\Gamma_6$ doublet is the ground state (fourth-order parameter $c$ is negative) in $CaF_2$, $ThO_2$, and $CeO_2$, which is also analogous to gadolinium in these crystals. The distinguishing features of the paramagnetic resonance of curium, as opposed to gadolinium, are: the larger departure of the Landé factor from 2 and the larger ground-state splitting in all five crystals [$LaCl_3$ and $La(C_2H_5SO_4)_3\cdot9H_2O$, where the crystal field has axial symmetry and $CaF_2$, $ThO_2$, and $CeO_2$, where the crystal field for the sites studied had cubic symmetry]. This is a clear indication that the ground state is not a pure $^8S_{7/2}$ state and that there is considerable admixture of non-$S$-state levels.

## ACKNOWLEDGMENT

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