

Lawrence Berkeley National Laboratory

LBL Publications

Title

Spectroscopic Study and Crystal Field Analysis of $\text{Cm}^{\text{3+}}$ in the Cubic Symmetry Site of ThO_2

Permalink

<https://escholarship.org/uc/item/7sd7k7wf>

Journal

Physical Review B, 50(14)

Authors

Thouvenot, P.
Hubert, S.
Edelstein, Norman M.

Publication Date

1994-04-21



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Submitted to Physical Review B

Spectroscopic Study and Crystal Field Analysis of Cm^{3+} in the Cubic Symmetry Site of ThO_2

P. Thouvenot, S. Hubert, and N. Edelstein

April 1994



LOAN COPY
Circulates
for 4 weeks

Bldg. 50 Library
Copy 2

LBL-35505

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**Spectroscopic Study and Crystal Field Analysis of Cm^{3+}
in the Cubic Symmetry Site of ThO_2**

P. Thouvenot, S. Hubert, and N. Edelstein

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

April 1994

Spectroscopic Study and Crystal Field Analysis of
 Cm^{3+} in the Cubic Symmetry Site of ThO_2

P. Thouvenot and S. Hubert

Laboratoire de Radiochimie, Institut de Physique Nucleaire, Boite Postale No. 1,
91406 Orsay, France

N. Edelstein

Lawrence Berkeley Laboratory, Chemical Sciences Division, University of California,
Berkeley, CA 94720

Abstract

Fluorescence and excitation spectra of Cm^{3+} diluted in ThO_2 powder are reported at room and low temperatures. The observed Cm^{3+} spectra are from the cubic symmetry lattice site and are assigned to phonon-assisted electric dipole transitions and to magnetic dipole transitions. From these assignments the crystal field parameters $B_0^4 = -6436 \text{ cm}^{-1}$ and $B_0^6 = 1195 \text{ cm}^{-1}$ have been determined. The experimental energy levels for the ground term ($\sim 80\% \text{ } ^8\text{S}_{7/2}$) determined from the optical data and earlier electron paramagnetic resonance spectra are in good agreement with the calculated values.

INTRODUCTION

Cm , element number 96 in the Periodic Table, occurs in the center of actinide series and its trivalent ion, Cm^{3+} (radon core, $5f^7$) has a half-filled shell. The differences in the electronic structure between the lanthanide counterpart Gd^{3+} , $4f^7$, and Cm^{3+} demonstrate the effect of the much greater spin-orbit coupling that occurs in the $5f$ series. The Gd^{3+} ground electronic term is an almost pure $^8\text{S}_{7/2}$ configuration. Although this

$J=7/2$ ion splits in a crystalline field into at most four doublets, the total extent of the splitting is on the order of $\sim 0.5 \text{ cm}^{-1}$. The Cm^{3+} ion has a much larger spin-orbit coupling constant and its ground term is only $\sim 80\%$ $^8\text{S}_{7/2}$. As a consequence of the mixing of higher-lying states into the ground term by the spin-orbit coupling interaction (intermediate coupling), the ground state splitting of the lowest $J=7/2$ state of Cm^{3+} in solids is considerably larger than in Gd^{3+} , $\sim 2 - 50 \text{ cm}^{-1}$.¹ The first correct report of the electron paramagnetic resonance (EPR) spectrum of Cm^{3+} was in $\text{Cm}^{3+}/\text{LaCl}_3$ system where the strongest resonance was assigned to a $J_z=1/2$ level and assumed to be the ground state.² Carnall recently reanalyzed the available optical data on $\text{Cm}^{3+}/\text{LaCl}_3$ and predicted a $\mu = 5/2$ level as the ground state in contradiction to the EPR data.³ High-resolution optical measurements by Liu *et al* on $\text{Cm}^{3+}/\text{LaCl}_3$ show that the total splitting of the nominally $^8\text{S}_{7/2}$ state in LaCl_3 is 1.97 cm^{-1} and that the ground doublet is indeed a $\mu = 5/2$ level.⁴ This doublet is EPR silent and with the ground term having a total splitting of 1.97 cm^{-1} , it was not possible to obtain reliable intensity measurements as a function of temperature in the earlier EPR experiment.² Since the optical analysis of $\text{Cm}^{3+}/\text{LaCl}_3$ gives a fit of $\sigma = 20 \text{ cm}^{-1}$ (σ is the rms deviation) for 65 levels it may be fortuitous that in fact the parameters predict the correct doublet ground state, and indeed the correct ordering of the four doublets that comprise the ground term for a term with that is split only by 1.97 cm^{-1} . Calculations predict a splitting of approximately $\sim 7.5 \text{ cm}^{-1}$.³

Similar results have been found in the $\text{Cm}^{3+}/\text{LuPO}_4$ system. Here the total splitting of the ground term is 12 cm^{-1} from EPR measurements.⁵ Analysis of the optical data is in progress, but the ordering of levels for the ground term is consistent with the EPR results.⁶ EPR measurements of Cm^{3+} in cubic host materials such as the alkaline earth fluorides, CeO_2 , and ThO_2 show much larger zero field splittings of the ground $J=7/2$ term. Analyses of the spectra indicate total splittings of $\sim 40 \text{ cm}^{-1}$ for $\text{Cm}^{3+}/\text{CaF}_2$ and greater than 15 cm^{-1} for $\text{Cm}^{3+}/\text{ThO}_2$.^{1,7}

In an earlier paper ⁸, the analysis of the optical spectra of low concentrations of Am³⁺ (< 0.1%) diluted in powdered samples of ThO₂, showed optical spectra only from the trivalent 5f⁶ Am³⁺ ion at the cubic symmetry site assigned to magnetic dipole and phonon- assisted electric dipole transitions. Optical measurements on Cm³⁺ in ThO₂ from selective excitation and fluorescence experiments are reported here and the crystal field parameters are derived from fitting these levels to an empirical Hamiltonian. These results are compared with other analyses of Cm³⁺ ions in various hosts.³⁻⁷

EXPERIMENTAL PROCEDURE

The ThO₂ sample doped with Cm³⁺ (0.05 at %) was synthesized as a powder following the method described previously ^{8,9}. To avoid any fluorescence quenching due to radiation damage, the isotope ²⁴⁸Cm ($\tau_{1/2} = 3.4 \times 10^5$ y) was used which has a much lower specific activity than the more common ²⁴⁴Cm ($\tau_{1/2} = 18.1$ y). The fluorescence and excitation spectra were recorded at room and liquid helium temperatures and analyzed with a 1-m JOBIN-YVON monochromator with a dispersion of 8 Å/mm. The fluorescence was detected with a R636 Hamamatsu photomultiplier. The sample was placed in a liquid helium cryostat (OXFORD Instruments) and excited with a LAMBDA-PHYSIK dye laser (pulse length 7ns and linewidth 0.1 cm⁻¹) pumped by a nitrogen laser. This experimental setup was controlled by a PC.

The Cm³⁺/ThO₂ sample exhibited an intense red fluorescence under short wavelength UV excitation (254 nm with a Hg lamp, or 337.1 nm with a N₂ laser) at room and low temperature. Excitation spectra at room temperature and 10 K were obtained in the visible region by monitoring the emission line at 6260Å. These spectra were obtained using several dyes (BBQ, BIS-MSB, DPS, Coumarin 440, 460, 480, 500, and Rhodamine 590 and 610).

EXPERIMENTAL RESULTS AND ANALYSIS OF THE SPECTRA

In a crystal field of O_h symmetry, the crystal field levels of trivalent curium are described by the group labels Γ_6 , Γ_7 and Γ_8 , where Γ_6 and Γ_7 are each doubly degenerate and Γ_8 is fourfold degenerate.¹⁰ All the states will be referred to either by these labels and/or by the free-ion J states. In this symmetry the f-f electric-dipole transitions are forbidden, while the f-f magnetic dipole transitions and the phonon-assisted electric dipole transitions are allowed. Thus as was the case for Am^{3+}/ThO_2 ⁸, strong, broad vibronic structure as well as sharp magnetic dipole transitions are observed.

A. Fluorescence spectra

At room temperature the fluorescence spectrum exhibits a large band between 6000 and 6500 Å (15400 cm^{-1} - 16600 cm^{-1}) (see Fig 1) corresponding to the magnetic dipole transition from the first excited state (${}^6D_{7/2}, {}^6P_{5/2}$) to the ${}^8S_{7/2}$ ground state. The structure observed on each side of the intense line at 15969 cm^{-1} is attributed to vibronic transitions located at the energies differences corresponding to the vibronic modes of the matrix (97, 276, 356, 475 and 575 cm^{-1}) and are assigned to the IR active modes^{8,9}. As shown in Fig. 1, the emission spectrum at ~ 10K is due primarily to a doublet at 15984 cm^{-1} and 15969 cm^{-1} . These narrow lines correspond to magnetic dipole transitions coming from the first optically excited state at 15984 cm^{-1} to the ${}^8S_{7/2}$ ground state and to the second crystal field level at 15 cm^{-1} . The vibronic structure situated on the high energy side at room temperature disappears at low temperature. The Cm^{3+}/ThO_2 sample exhibits an intense red fluorescence under short wavelength UV excitation at room and low temperatures. On the low energy side of the strong fluorescence a weak band at 15878 cm^{-1} is observed which is located at 91 cm^{-1} from the zero phonon line and corresponds to a vibronic line. The assigned emission lines observed at 10K are presented

in Table I. Note that the transition from the ${}^6D_{7/2}$ excited level to the third crystal field level of the ground ${}^8S_{7/2}$ term is not observed in the emission spectrum.

B- Excitation spectra

The excitation spectra obtained in the visible region at ~ 10 K are shown in Figures 2 and 3. Numerous vibronic lines associated either with magnetic dipole transitions or with absent electric dipole transitions are observed. In the latter case, the assignments of the vibronic bands determine the energies of the forbidden 0-0 transitions. However unlike Am^{3+}/ThO_2 , many narrow lines from magnetic dipole transitions also were observed. The spectra are assigned on the basis of the Cm^{3+} ions occupying only a cubic symmetry site in agreement with the data for Am^{3+}/ThO_2 ⁸.

Although only the lowest component of the ${}^6D_{7/2}$ is found in the luminescence spectra at 15984 cm^{-1} , in the excitation spectrum between 16100 cm^{-1} and 16700 cm^{-1} , the second Stark level of the ${}^6D_{7/2}$ multiplet is observed at 16277 cm^{-1} , Fig. 2A. The third ${}^6D_{7/2}$ crystal field component appears in the region between 17400 cm^{-1} and 17700 cm^{-1} . At 10K, the two narrow lines at 17518 cm^{-1} and 17554 cm^{-1} correspond to transitions arising from the second excited level of the ground term at 36 cm^{-1} and from the ${}^8S_{7/2}$ ground state to the third Stark component of the ${}^6D_{7/2}$ term, Fig. 2B. In the excitation spectrum between 19100 cm^{-1} and 20000 cm^{-1} , two narrow doublets correspond to transitions coming from the ${}^8S_{7/2}$ ground state and the 15 cm^{-1} level to the ${}^6P_{5/2}$ state at 19315 cm^{-1} , and from the ground state and the 35 cm^{-1} level to the ${}^6P_{5/2}$ level at 19791 cm^{-1} , see Fig. 2C. The weak feature at 19263 cm^{-1} is unassigned.

In the region from 20660 cm^{-1} to 26500 cm^{-1} (Fig. 3), the excitation spectra become more complicated. Most of the features observed can be assigned to intense vibronic transitions associated with electric dipole transitions and to a few narrow lines associated with zero phonon magnetic dipole transitions. As in the analysis of the

optical spectra of $\text{Am}^{3+}/\text{ThO}_2$ ⁸, the zero phonon electric dipole transitions can be deduced from the vibronic assignments. Table II lists the energies of the zero phonon transitions with their associated vibronic lines. Sixteen excited states were assigned. The transitions involving the $^8\text{S}_{7/2}$ ground manifold allow the determination of the total splitting of the ground state. From the emission and excitation spectra, the crystal field splittings of the ground manifold are determined to be 0, 15, and 36 cm^{-1} .

DISCUSSION

The levels were fit by simultaneous diagonalization of the free-ion (H_{FI}) and crystal-field (H_{CF}) Hamiltonians:

$$\begin{aligned}
 H_{FI} = & \sum_{k=0,2,4,6} F^k(nf,nf) f_k + \zeta_f \alpha_{s.o.} + \alpha L(L+1) \\
 & + \beta G(G_2) + \gamma(R_7) + \sum_{\substack{k=2,8 \\ k \neq 5}} T^k t_k \\
 & + \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k
 \end{aligned}$$

and

$$\begin{aligned}
 H_{CF} = & B_0^4 [C_0^4 + (5/14)^{1/2} (C_{-4}^4 + C_4^4)] + \\
 & B_0^6 [C_0^6 - (7/2)^{1/2} (C_{-4}^6 + C_4^6)].
 \end{aligned}$$

The $F^k(nf,nf)$ and ζ_f parameters above represent the radial part of the electrostatic interaction between two f electrons, and the spin-orbit interaction, respectively, while f_k and $\alpha_{S.O}$ are angular parts of these interactions. The parameters α, β, γ are associated with

the two body effective operators of the configuration interaction, and the T^k s are the corresponding parameters of the three-body configuration interaction operators. The M^k parameters represent the spin-spin and spin-orbit interactions, and the P^k parameters arise from electrostatic-spin-orbit interactions with higher configurations. For O_h symmetry the crystal field interaction is parametrized by B_0^4 and B_0^6 and the angular operators of C_q^k are the Racah tensors. ¹¹

The crystal field parameters obtained earlier for Am^{3+}/ThO_2 ⁸ and the $Cm^{3+}/LaCl_3$ free ion parameters found by Carnall ³ were used initially for fitting the experimental levels. For the first fit, the crystal field parameters were held fixed, and F^2 , F^4 , F^6 and ζ were allowed to vary freely using 11 experimental levels. Then the four free ion parameters were fixed at the values which gave the minimum rms deviation between the calculated and experimental energy levels, and the crystal field parameters were varied. Further energy levels were assigned and finally the above four free ion parameters and the two crystal field parameters were varied simultaneously. The results of the fits and the final assignments of the experimental and calculated levels are given in Table III. The O_h symmetry labels were assigned on the basis of the calculated energy levels and wavefunctions. In the final fit 20 experimental levels were used and an rms deviation of 21.7 cm^{-1} was obtained. One experimental level from Table III (25620 cm^{-1}) was not used in the fit as it gave a much greater deviation than any other level. The calculated ground state g value of 4.513 is in good agreement with the experimental EPR g value of 4.484.

The crystal-field states of the ground manifold show good agreement between the calculated and experimental levels. The ground state is a Γ_6 level and the energy of the first excited state (Γ_8) is in agreement with the value obtained from EPR data. The energy splitting of $15.5 \mp 0.3 \text{ cm}^{-1}$ was determined from the magnitude of the anisotropy of the g value of the ground Γ_6 state caused by the magnetic field mixing between the $\Gamma_6 - \Gamma_8$ states.⁷ As pointed out by Edelstein *et al.*,¹ Carnall ³, and Liu *et al.*,⁴

the substantially increased spin-orbit coupling and reduced electrostatic interaction for 5f electrons results in a higher degree of admixture of excited states into the ground state when compared to Gd^{3+} . In this work the ground state wavefunction for Cm^{3+} is approximately 78% $^8S_{7/2}$ and 19% $^6P_{7/2}$. The empirical parameters found for Cm^{3+}/ThO_2 are given in Table IV and compared with the parameters for Am^{3+}/ThO_2 .⁸ As expected, the crystal-field parameters of the Cm^{3+} ion ($5f^7$) in ThO_2 are almost the same as for Am^{3+} ($5f^6$). The value of B_0^4 parameter is slightly smaller than it is for Am^{3+} , the B_0^6 is rather larger. However the crystal-field strength parameter N'_v defined elsewhere⁸, gives almost the same value for Cm^{3+} (2951 cm^{-1}) as for Am^{3+} (2945 cm^{-1}), as expected for ions which are neighbors in the Periodic Table.

In the emission spectrum, only two magnetic dipole transitions are observed. They originate from the first excited level at 15984 cm^{-1} to the first two first components of the $^8S_{7/2}$ ground state at 0 and 15 cm^{-1} . A third transition from the 15984 cm^{-1} level terminating at the third excited level (Γ_7) above the ground state was not observed in the fluorescence spectrum. Magnetic dipole intensity calculations for the transitions give the calculated intensities 1.58×10^{-3} and 4.8×10^{-3} for the transitions from the emitting state to the first two states of the ground manifold and 2.74×10^{-17} for the transition to the third state. Moreover the relative intensity of these two observed magnetic dipole transitions have approximately the same ratio as that calculated.

It is interesting to note that in all cases where an optical analysis of Cm^{3+} in a host matrix has been reported, the splittings predicted from the analyses reproduce the correct ordering of the states in the ground $^8S_{7/2}$ term.^{3,4,6} However in the present work the magnitudes of the splittings are approximately reproduced by the crystal field parameters. For Cm^{3+}/ThO_2 the total ground state splitting is 36 cm^{-1} as compared to a maximum of $\sim 12\text{ cm}^{-1}$ for the other hosts where all levels have been measured. In ThO_2 the crystal field is large enough so that the Cm^{3+} ground state splittings due to intermediate coupling effects are dominant over other splitting mechanisms. Thus the conventional crystal field

model can reproduce the observed splittings of the ground state and the excited states in a satisfactory way.

CONCLUSION

The fluorescence and excitation spectra of Cm^{3+} have been assigned. The crystal-field parameters were obtained by fitting the 20 levels deduced either from magnetic dipole transitions or from phonon-assisted electric dipole transitions. The optical data for the ground state splittings are in very good agreement with levels obtained earlier from EPR measurements. While the fourth order crystal-field parameter B_0^4 is almost the same as found for Am^{3+} , the sixth-order parameter is larger for Cm^{3+} than Am^{3+} . However the magnitude of the sixth order parameter is still much smaller than that found from neutron diffraction experiments on the UO_2 , NpO_2 and PuO_2 .⁸

ACKNOWLEDGMENTS

This research was sponsored in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors are indebted, for the use of ^{248}Cm , to the Division of Chemical Sciences, Office of Basic Energy Sciences, through the transplutonium element production facilities at Oak Ridge National Laboratory.

REFERENCES

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

2. M. M. Abraham, B. R. Judd, and H. Wickman, *Phys. Rev.* **130**, 611 (1963).
3. W. T. Carnall, *J. Chem. Phys.* **96**, 8713 (1992).
4. G. K. Lui, J. V. Beitz, and J. Huang, *J. Chem. Phys.* **99**, 3304 (1993).
5. W. K. Kot, N. Edelstein, M. M. Abraham, and L. A. Boatner, *Phys. Rev.* **B48**, 12704 (1993).
6. J. Sytsma, N. Edelstein, M. M. Abraham, and L. A. Boatner (manuscript in preparation).
7. W. Kolbe, N. Edelstein, C. B. Finch and M. M. Abraham, *J. Chem. Phys.* **56**, 5432(1972); *J. Chem. Phys.* **58**, 820(1973).
8. S. Hubert, P. Thouvenot and N. Edelstein, *Phys. Rev.* **B48**, 5751(1993).
9. S. Hubert and P. Thouvenot, *J. Lum.* **54**, 103(1992).
10. G. F. Koster, J. O. Dinnock, R. G. Wheeler, and H. Statz, "Properties of the Thirty-Two Point Groups," M.I.T. Press, Cambridge, MA, 1963.
11. W.T. Carnall, H. Crosswhite, H.M. Crosswhite, J.P. Hessler, N.M. Edelstein, J.G. Conway, G.V. Shalimoff and R. Sarup, *J. Chem. Phys.* **72**, 5089(1980).

Table I -Zero-phonon and phonon-assisted transitions energies from the luminescence spectrum at 10 K

Wavelength $\lambda(\text{\AA})$	Energy (cm^{-1})	Transitions	ΔE^a (cm^{-1})	ΔE^b (cm^{-1})
6225	16060		91	
6254.5	15984	${}^6D_{7/2} \rightarrow {}^8S_{7/2}$	0	0
6260.5	15969	${}^6D_{7/2} \rightarrow {}^8S_{7/2}$	0	15
6290.5	15893		90	
6369	15695		274	
6445	15512		457	
6489	15407		562	

^a Energy differences between the zero-phonon transition and phonon-assisted transitions

^b Energy differences between the Stark levels of the ${}^8S_{7/2}$ ground state

Table II- Energies of zero-phonon and phonon-assisted transitions from excitation spectra at 10K

Wavelength $\lambda(\text{\AA})$	Energy (cm^{-1})	Transitions ${}^8S_{7/2} \rightarrow$	ΔE^a (cm^{-1})	ΔE^b (cm^{-1})
6142	16277	${}^6D_{7/2}$		11
6138	16288	${}^6D_{7/2}$	0	
5707	17518	${}^6D_{7/2}$		36
5695	17554	${}^6D_{7/2}$	0	
5190	19263			52 ^c
5180	19300	${}^6P_{5/2}$		15
5176	19315	${}^6P_{5/2}$	0	
5060.5	19756	${}^6P_{5/2}$	0	35
5051.5	19791	${}^6P_{5/2}$	0	
4807	20797	${}^6I_{7/2}$		15
4803.5	20812	${}^6I_{7/2}$	0	
4783	20902		90	
4740	21090		278	
4675	21383		571	
4774.5	20939	${}^6I_{7/2}$		17
4770.5	20956	${}^6I_{7/2}$	0	
4749	21051		95	
4709	21230		274	
4669	21412		456	
4643	21532		576	
4599	21738	${}^6I_{7/2}$	0	
4581	21823		93	
4544	22001		271	

Table II (continued)

Wavelength λ (Å)	Energy (cm^{-1})	transitions ${}^8S_{7/2} \rightarrow$	ΔE^a (cm^{-1})	ΔE^b (cm^{-1})
4504	22196		466	
4483	22300		570	
4565.5	21897	${}^6I_{9/2}$		36
4558	21933	${}^6I_{9/2}$	0	
4538	22030		97	
4505	22203		270	
4464.5	22405		464	
4442	22506		573	
4367	22890		92	
4357	22946	${}^6I_{9/2}$		36
4350	22982	${}^6I_{9/2}$	0	
4347	22997 ^d			
4333	23073		91	
4297.5	23263		281	
4265	23440		458	
4243	23562		580	
(4198)	(23815)	${}^6I_{11/2}$	0	
4181	23912		97	
4150	24090		275	
(4176)	(23940)	${}^4I_{17/2}$	0	
4159	24036		97	
4128.5	24215		275	
4099	24390		450	
4078	24516		576	

Table II - (end)

Wavelength λ (Å)	Energy (cm^{-1})	Transitions ${}^8S_{7/2} \rightarrow$	ΔE^a (cm^{-1})	ΔE^b (cm^{-1}) (cm^{-1})
(4109)	(24330)	${}^4I_{17/2}$	0	
4063.5	24603		273	
4033	24789		459	
4015	24901		571	
4046	24710	${}^6D_{9/2}$	0	
(3943)	(25353)	${}^6I_{13/2}$	0	
3901	25628		275	
3888	25710		357	
3873.5	25808		455	
3853	25946		593	
(3929)	(25444)	${}^6I_{13/2}$	0	
3887	25718		274	
3873.5	25808		365	
3860	25900		456	
3840	26034		591	
(3902)	(25620) ^{c,e}		0	
3887	25718		98	
3860	25899		279	
3834	26074		454	
3816	26195		575	
3825.5	26132	${}^6D_{9/2}$	0	
3813	26218		84	

^a Energy differences between the zero-phonon line and vibronic lines

^b Energy differences between the ${}^8S_{7/2}$ ground state multiplets

^c Not assigned

^d Shoulder, not assigned

^e Not used in the fitting procedure

Table III - Calculated and experimental energy levels for $\text{Cm}^{3+}/\text{ThO}_2$

Level	Largest S-L-J comp.	Calc. energy (cm^{-1})	Expt. energy (cm^{-1})	$\Delta(E_{\text{exp}} - E_{\text{calc}})$ (cm^{-1})
1 Γ_6	$^8\text{S}_{7/2}$	-1.7	0	1.7
1 Γ_8	$^8\text{S}_{7/2}$	10.8	15	4.2
1 Γ_7	$^8\text{S}_{7/2}$	40.8	36	-4.8
2 Γ_6	$^6\text{D}_{7/2}$	16025.9	15984	-41.9
2 Γ_8	$^6\text{D}_{7/2}$	16255.0	16288	33.0
2 Γ_7	$^6\text{D}_{7/2}$	17568.7	17554	-14.7
3 Γ_8	$^6\text{P}_{5/2}$	19314.2	19315	.0.8
3 Γ_7	$^6\text{P}_{5/2}$	19792.7	19791	-1.7
3 Γ_6	$^6\text{I}_{7/2}$	20831.4	20812	-19.4
4 Γ_8	$^6\text{I}_{7/2}$	20938.9	20956	17.1
5 Γ_8	$^6\text{P}_{3/2}$	21450.3		
4 Γ_7	$^6\text{I}_{7/2}$	21709.0	21738	29.0
4 Γ_6	$^6\text{I}_{9/2}$	21910.0	21933	23.0
6 Γ_8	$^6\text{I}_{9/2}$	22097.2		
7 Γ_8	$^6\text{I}_{9/2}$	22973.3	22982	8.7
5 Γ_7	$^6\text{I}_{11/2}$	23689.9		
8 Γ_8	$^6\text{I}_{11/2}$	23818.4	23815	-3.4
9 Γ_8	$^6\text{I}_{17/2}$	23940.5	23940	-0.5
5 Γ_6	$^6\text{I}_{17/2}$	24034.5		
10 Γ_8	$^6\text{I}_{17/2}$	24089.2		
11 Γ_8	$^6\text{I}_{17/2}$	24289.1		
6 Γ_6	$^6\text{I}_{17/2}$	24340.3	24330	-10.3
6 Γ_7	$^6\text{I}_{17/2}$	24374.6		
12 Γ_8	$^6\text{I}_{17/2}$	24669.8		
13 Γ_8	$^6\text{I}_{17/2}$	24729.8	24710	-19.8
7 Γ_7	$^6\text{I}_{13/2}$	24847.6		
7 Γ_6	$^6\text{I}_{11/2}$	24868.4		
14 Γ_8	$^6\text{I}_{13/2}$	24976.6		
8 Γ_6	$^6\text{I}_{15/2}$	25184.0		
15 Γ_8	$^6\text{I}_{15/2}$	25288.6		
8 Γ_7	$^6\text{I}_{13/2}$	25305.7		

Table III (end)

Level	Largest S-L-J comp.	Calc. energy (cm ⁻¹)	Expt. energy (cm ⁻¹)	$\Delta(E_{\text{exp}} - E_{\text{calc}})$ (cm ⁻¹)
9 Γ_6	$6^1_{13/2}$	25329.0		
9 Γ_7	$6^1_{13/2}$	25346.9	25353	6.1
16 Γ_8	$6^1_{13/2}$	25434.9	25444	9.1
17 Γ_8	$6^1_{15/2}$	25773.5		
18 Γ_8	$6^1_{15/2}$	25906.3		
10 Γ_6	$6^1_{9/2}$	26148.1	26132	-16.1
19 Γ_8	$6^1_{9/2}$	26195.8		
10 Γ_7	$6^1_{7/2}$	27149.4		
11 Γ_6	$6^1_{7/2}$	27489.8		
20 Γ_8	$6^1_{7/2}$	27502.9		

Table IV- Values of the spectroscopic parameters

Parameters	$\text{Am}^{3+}/\text{ThO}_2^{\text{a}}$ (cm^{-1})	$\text{Cm}^{3+}/\text{ThO}_2^{\text{b}}$ (cm^{-1})
F^2	48038.0(140.2)	50523.6(102.4)
F^4	39684.2(212.9)	47933.9(130.2)
F^6	29574.1(171.4)	29271.3(83.8)
ζ	2511.1(27.0)	2691.1(14.1)
α	33.2(8.6)	[28.3]
β	[-660]	[-650]
γ	[1000]	[825]
T^2	[200]	[200]
T^3	[50]	[50]
T^4	[40]	[40]
T^6	[-360]	[-360]
T^7	[390]	[390]
T^8	[340]	[340]
M^0	[0.99]	[1.09]
M^2	[0.55]	[0.61]
M^4	[0.38]	[0.41]
P^2	[850]	[912]
P^4	[637.5]	[684]
P^6	[425]	[456]
B_0^4	-6731.3(96.0)	-6446.5(42.6)
B_0^6	713.6(115.0)	1142.1(32.1)

^a From Reference 8. All parameters values in [] held fixed in the fitting procedure

^b 20 experimental levels, rms deviation 21.7 cm^{-1}

Figure Captions

Figure 1. Room temperature and low temperature fluorescence of $\text{Cm}^{3+}/\text{ThO}_2$.

Figure 2. Excitation spectra of $\text{Cm}^{3+}/\text{ThO}_2$ at 10K. A. 16100 - 16700 cm^{-1} region; B. 17400 - 17700 cm^{-1} region showing the crystal field splitting between the first (lowest) and the third crystal field level of the ground term; C. 19100 - 20000 cm^{-1} region showing the splitting between the first and second crystal field levels of the ground term ($\sim 19300 \text{ cm}^{-1}$) as well as the splitting between the first and third levels ($\sim 19790 \text{ cm}^{-1}$).

Figure 3. Excitation spectra of $\text{Cm}^{3+}/\text{ThO}_2$ at 10K between 20600 and 26300 cm^{-1} .

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720

