Lawrence Berkeley National Laboratory

Recent Work

Title

OPTICAL SPECTROSCOPY AND ELECTRON PARAMAGNETIC RESONANCE OF Pa^{4+} IN ThBr_4 AND ThCl_4 CRYSTALS

Permalink

<https://escholarship.org/uc/item/32128869>

Author

Krupa, J.C.

Publication Date

1982-10-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 9 1983

LIBRARY AND
DOCUMENTS SECTION

Submitted to Journal of Chemical Physics

OPTICAL SPECTROSCOPY AND ELECTRON PARAMAGNETIC
RESONANCE OF Pa^{4+} IN ThBr_4 AND ThCl_4 CRYSTALS

J.C. Krupa, S. Hubert, M. Foyentin,
E. Gamp, and N. Edelstein

October 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LBL-15084
c.2

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.

LBL-15084

Optical Spectroscopy and Electron Paramagnetic Resonance
of Pa^{4+} in ThBr_4 and ThCl_4 Crystals

J.C. Krupa, S. Hubert, M. Foyentin
Laboratoire de Radiochimie, Institut de Physique Nucleaire
Universite de Paris-Sud, B.P. No. 1
91406 Orsay Cedex, France

and

E. Gamp and N. Edelstein
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 USA

October 1982

Abstract

Polarized absorption and emission spectra of Pa^{4+} in ThCl_4 and ThBr_4 host matrices were recorded at different temperatures from 4.2K to 300K in the infrared range. The seven crystal field levels of the $5f^1$ configuration were determined from the optical data and fit by a parametrized model assuming a D_{2d} site symmetry for the Pa^{4+} ion. However at low temperature both matrices undergo a displacive phase transition and the low temperature structure is incommensurate and modulated. The halide position modulation reduces the site symmetry from D_{2d} to D_2 for some Pa^{4+} ions, and consequently the shapes of some absorption bands are characterized by edge singularities. EPR experiments performed on these doped crystals provided g values for the ground state of Pa^{4+} which fit satisfactorily with the values calculated from the optical data.

I. Introduction

Thorium tetrabromide and thorium tetrachloride are new host lattices for the study of tetravalent actinide ions, and in some cases trivalent lanthanide ions, by optical spectroscopy.¹⁻³ At room temperature both crystals have a D_{4h}^{19} tetragonal structure isostructural with UCl_4 .⁴⁻⁶ In this structure, the Th^{4+} ions are at a site of D_{2d} symmetry and other tetravalent actinide ions can substitute into this site. Recently a displacive phase transition was observed by Raman scattering spectroscopy⁷ and nuclear quadrupole resonance⁸ at 95K for $ThBr_4$ and 70K for $ThCl_4$. Single crystal neutron diffraction experiments on $ThBr_4$ revealed that the low temperature structure is incommensurate with a modulation along the four-fold axis.⁹ Below the transition temperature, the sinusoidal distortion which modulates the Br ion positions reduces the actinide ion site symmetry from D_{2d} to D_2 .¹⁰ However it has been shown from spectral singularities of $U^{4+}:ThBr_4$ by absorption spectroscopy that some of the impurity ions pin the phase of the modulation and are in D_{2d} sites.

Optical spectroscopy studies of Pa^{4+} in $ThBr_4$ have been undertaken to further study the crystal field effects of the incommensurate structure on the $5f^1$ configuration and to compare the derived parameters with earlier work on Pa^{4+} in $ThCl_4$.³ Electron paramagnetic resonance (EPR) studies described in this paper provide information about the ground state of Pa^{4+} diluted in $ThCl_4$ and $ThBr_4$. The results of these measurements will be discussed here.

II. Experimental

The syntheses and the growth of single crystals of ThCl_4 and ThBr_4 have been reported previously.^{3,11} Pa_2O_5 purchased from AERE, Harwell, was added to the thorium tetrahalides at about 0.1 wt percent. The mixture was melted and then passed through the furnace at a rate of 5mm per day. For optical studies the resulting crystals were cut in an inert atmosphere box and oriented with the four-fold axis perpendicular to one face. After the crystals were polished, they were sealed in a silica tube under 300 Torr of helium. For the EPR experiments powdered samples were placed in a 3mm inner diameter high-purity silica tube and sealed under vacuum.

The absorption and emission spectra were obtained with the instruments described previously.³ Variable temperature spectra were recorded between 4.2 and 300K using a helium-gas-circulating cryostat. X-band EPR spectra (~ 9.1 GHz) on the powdered samples were obtained at ~ 10 -15K using a Varian E-12 spectrometer equipped with an Air Products Helitran cooling system. The microwave frequency was monitored with a transfer oscillator and a frequency counter, and the magnetic field with a proton nuclear magnetic resonance gaussmeter.

III. Experimental Results

A. Optical Spectra

The absorption and emission spectra of $\text{Pa}^{4+}:\text{ThBr}_4$ closely resembled the spectra previously reported for $\text{Pa}^{4+}:\text{ThCl}_4$.³ At 77K, four absorption bands were observed between 1480nm and 1870nm for

$\text{Pa}^{4+}:\text{ThCl}_4$ and between 1540nm and 1870nm for $\text{Pa}^{4+}:\text{ThBr}_4$ (see Figures 1 and 2). These bands have been assigned to transitions from the ground crystal field state of the $J=5/2$ multiplet to the four crystal field states of the excited $J=7/2$ multiplet. At 4.2K, the structure of the absorption bands is more complex. In addition to the strong zero-phonon absorption bands whose shapes are characterized by edge singularities,¹⁰ there are less intense peaks on the high energy side which are vibronic bands related to the normal mode vibrations of the matrix.

The peculiar line shapes for the zero-phonon transitions can be explained by the incommensurate structure of the host crystal, ThBr_4 , below 95K. In the pure material, the sinusoidal modulation of the Br ion positions along the four-fold high symmetry axis reduces the metal ion site symmetry from D_{2d} to D_2 . In the diluted crystal, the Pa^{4+} impurity forces the local symmetry (at some Pa^{4+} sites) to remain D_{2d} . Therefore the symmetry at the Pa^{4+} sites varies from D_{2d} at one extreme to the maximum D_2 distortion at the other. The line shape then follows a continuous variation which reflects the shift of the energy levels as the symmetry changes.¹⁰ This variation is shown in Fig. 3 for the π spectra (E||C) and can be described as a continuum of absorption lines between two sharp edges. Similar peak shapes were obtained for $\text{Pa}^{4+}:\text{ThCl}_4$ which confirms the postulated modulated structure for this host material as determined by nuclear quadrupole resonance spectroscopy.⁸

A striking feature of the optical spectra of Pa^{4+} in these

hosts is the strong, temperature-sensitive fluorescence. This fluorescence is quenched at a temperature of $\sim 110\text{K}$ for ThCl_4 and $\sim 100\text{K}$ for ThBr_4 . A less intense fluorescence line at lower energy is also observed in both crystals. Selective excitation experiments separately exciting each of the four doublets of the $J=7/2$ excited state resulted in the exactly same fluorescence pattern. Such behaviour means the lowest doublet of the $J=7/2$ state is fed non-radiatively from the upper states and all the fluorescence originates in this lowest doublet. The observation of the fluorescence spectrum allows the splitting of the $J=5/2$ state to be determined unambiguously.

A temperature-dependent line in the absorption spectra was measured for Pa^{4+} in both host matrices. This line appears at 1714nm for ThCl_4 and 1753nm for ThBr_4 . The area of this peak versus temperature followed the Boltzman population distribution so this peak was assigned as the transition from the first excited state above the ground crystal field state to the highest Γ_6 state of the $J=7/2$ multiplet. The energy level diagrams obtained from the optical spectra of $\text{Pa}^{4+}:\text{ThBr}_4$ and $\text{Pa}^{4+}:\text{ThCl}_4$ are given in Figure 4 and Table 1 where the states are labelled by the irreducible representations of the D_{2d} double group.

The assignments of the transitions classified as $\Gamma_6 \rightarrow \Gamma_6$ under D_{2d} symmetry were confirmed by the measurements of the polarized spectra as shown in Table 1. However for transitions classified as $\Gamma_6 \rightarrow \Gamma_7$ in D_{2d} symmetry, both σ and π polarizations are allowed. As mentioned previously, the modulated structure of the host

crystals causes a continuous variation of some of the sites of Pa^{4+} from D_{2d} to the limiting D_2 symmetry. In D_2 symmetry both σ and π transitions are allowed so the polarization experiments did not distinguish between D_2 and D_{2d} site symmetries. For these bands, the weaker feature of the absorption spectrum was assigned to the D_{2d} site for the following reason. The lower symmetry of the D_2 site causes additional mixing of even parity excited configurations, which should result in the absorption lines from the lower symmetry site being more intense than from the D_{2d} site. However, even if one of the $\Gamma_6 \rightarrow \Gamma_7$ transitions is misassigned, the linewidth of the band (representing the energy difference between the D_{2d} and the most extreme D_2 site) is $\sim 50 \text{ cm}^{-1}$. This misassignment would have only a small effect on the parameters obtained from fitting the optical spectra.

B. EPR Spectra

The EPR spectra of powders of $\text{Pa}^{4+}:\text{ThBr}_4$ and $\text{Pa}^{4+}:\text{ThCl}_4$ are shown in Fig. 5A and Fig. 6A and clearly show that the g and A tensors are almost isotropic. The parameters of the spin-Hamiltonian,

$$H = g_{\parallel} \beta H_z S_z' + g_{\perp} \beta (H_x S_x' + H_y S_y') + A_{\parallel} S_z' H_z + A_{\perp} (S_x' I_x + S_y' I_y)$$

where $S' = 1/2$ and $I = 3/2$ for ^{231}Pa , were obtained by simulation of the spectra¹² and are given in Table 2. It has been assumed the quadrupole interaction is negligible. The calculated spectra are shown in Fig. 5B and Fig. 6B and were obtained assuming a Lorentzian line shape and an isotropic line width of 20 gauss for $\text{Pa}^{4+}:\text{ThCl}_4$ and 40 gauss for $\text{Pa}^{4+}:\text{ThBr}_4$. The fact that relatively narrow line widths are found for these samples suggests that the deviations from D_{2d} symmetry do not greatly affect the magnetic properties of the ground state. Nevertheless, the experimental spectra, especially $\text{Pa}^{4+}:\text{ThCl}_4$, show a marked anisotropy of the line width which increased when the magnetic field is perpendicular to the highest symmetry axis. The increase in line width in this plane could be due to the decrease in symmetry from D_{2d} to D_2 for the modulated structure which should split g_z into g_x and g_y . Attempts to simulate the powder spectrum with an orthorhombic g and A tensor were unsatisfactory. Single crystal EPR data for the x,y -plane are necessary to confirm the above hypothesis. The only other report of EPR of Pa^{4+} has been given by Axe, Stapleton and Jeffries for octahedral symmetry in the host crystal Cs_2ZrCl_6 .¹²

IV. Calculations and Discussion

The assigned spectra were fit by a least-squares routine to the parameters of the following Hamiltonian which, for an f^1 configuration, included only the spin-orbit coupling interaction and a crystal field of D_{2d} symmetry:^{3,14}

$$H = H_{S.O.} + H_{C.F.}$$

where

$$H_{S.O.} = \xi \vec{l} \cdot \vec{s}$$

and

$$H_{C.F.} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_4^4 (C_4^4 + C_{-4}^4) + B_4^6 (C_4^6 + C_{-4}^6).$$

The spin-orbit coupling constant and the diagonal crystal field parameters initially were allowed to vary using as starting parameters the values of the crystal field parameters obtained from $U^{4+}:\text{ThCl}_4$ and $U^{4+}:\text{ThBr}_4$.¹⁵ Finally, various sets of the empirical parameters were varied until the difference between the calculated and experimental energies reached a minimum. The best fit resulted in an r.m.s. deviation for seven levels of 23.6 cm^{-1} for $\text{Pa}^{4+}:\text{ThCl}_4$ and 19.4 cm^{-1} for $\text{Pa}^{4+}:\text{ThBr}_4$. The calculated energy levels are also shown in Table 1 and the two sets of empirical parameters are given in Table 3.

As one would expect from the structure of the host crystals, the crystal field parameters of the $\text{Pa}^{4+}:\text{ThCl}_4$ are larger than for $\text{Pa}^{4+}:\text{ThBr}_4$, except perhaps in the case of the poorly determined values of B_4^6 . The spin-orbit coupling constants for the two hosts are the same within the experimental accuracy and very close to

those found by H.D. Amberger for PaCl_4 .¹⁶ A further test of these parameters can be made by the calculation of the ground state $g_{\parallel}$ and $g_{\perp}$ values. Table 4 lists the ground state wavefunctions for the 2F L-S terms in the $|JJ_z\rangle$ representation and the calculated values of $g_{\parallel}$ and $g_{\perp}$. Although the experimental values are $|g_{\parallel}| \cong |g_{\perp}| \cong 1.6$, considering the great sensitivity of the g values to the wavefunctions (the calculation of g values is a much more severe test of the wavefunctions than the fitting of energy levels) and the fact that no extra parameters such as the orbital reduction factor were utilized, the agreement must be considered quite satisfactory. Finally, the effect of J mixing in these crystals is quite small; for the ground state of $\text{Pa}^{4+}:\text{ThBr}_4$ the wavefunction is 99.7 percent $^2F_{5/2}$, while for $\text{Pa}^{4+}:\text{ThCl}_4$, the wavefunction is 99.8 percent $^2F_{5/2}$.

The analysis given here and in the earlier paper satisfactorily fit the optical and EPR spectra. The only ambiguity arises from the fact that at low temperature there is a question, due to the incommensurate structure, about which feature of one $\Gamma_6 \rightarrow \Gamma_7$ absorption band should be assigned to Pa^{4+} in a D_{2d} symmetry site.

Acknowledgements

This work was supported 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.

TABLE I

List of Experimental and Calculated Energies

L-S State	$\text{Pa}^{4+}:\text{ThCl}_4$		$\text{Pa}^{4+}:\text{ThBr}_4$		Irreducible Representation
	Obs. (cm^{-1})	Calc. (cm^{-1})	Obs. (cm^{-1})	Calc. (cm^{-1})	
$2F_{5/2}$	0	21.8	0	19.9	Γ_6
	423	408.8	322	313.9	Γ_7
	1260	1252.7	954	940.5	Γ_6
$2F_{7/2}$	5338	5312.4	5344	5324.3	Γ_6
	5590	5605.8	5517	5522.6	Γ_7
	6286	6291.3	6021	6026.0	Γ_6
	6711	6715.1	6458	6464.8	Γ_7

TABLE II

Parameters of the Spin-Hamiltonian ($\nu \sim 9.15$ GHz)

	$ g_{\parallel} $	$ g_{\perp} $	$A_{\parallel}(\text{cm}^{-1})$	$A_{\perp}(\text{cm}^{-1})$
$\text{Pa}^{4+}:\text{ThCl}_4$	1.605	1.574	0.0556	0.0626
$\text{Pa}^{4+}:\text{ThBr}_4$	1.616	1.616	0.0571	0.0636

TABLE III

Spin-Orbit and Crystal Field Parameters
Obtained by Fitting the Optical Data

Parameters ^a	Pa ⁴⁺ :ThCl ₄ (cm ⁻¹)	Pa ⁴⁺ :ThBr ₄ (cm ⁻¹)
ξ	1524.2 ± 5	1532.8 ± 5
B_0^2	-1404.8 ± 50	-1046.5 ± 52
B_0^4	1749.4 ± 94	1366.3 ± 138
B_4^4	-2440.3 ± 98	-1990.1 ± 102
B_0^6	-2404.2 ± 607	-1162.0 ± 541
B_4^6	-194.5 ± 267	623.1 ± 174

^aThese sets of parameters are obtained for $F^0 = 3658 \text{ cm}^{-1}$ for Pa⁴⁺:ThCl₄ and $F^0 = 3516 \text{ cm}^{-1}$ for Pa⁴⁺:ThBr₄.

TABLE IV

Ground State Wave Functions and
Calculated g Values^a

$$\text{Pa}^{4+}:\text{ThCl}_4 \quad .9092 |5/2, 3/2\rangle + .4005 |5/2, -5/2\rangle + .0448 |7/2, 3/2\rangle \\ + .1050 |7/2, -5/2\rangle$$

$$g_{\parallel} = -1.249 \qquad |g_{\perp}| = 1.201$$

$$\text{Pa}^{4+}:\text{ThBr}_4 \quad .9062 |5/2, 3/2\rangle + .4198 |5/2, -5/2\rangle + .0087 |7/2, 3/2\rangle \\ + .0505 |7/2, -5/2\rangle$$

$$g_{\parallel} = -1.296 \qquad |g_{\perp}| = 1.381$$

^a $|J, J_z\rangle$ Representation

References

1. M. Genet, P. Delamoye, N. Edelstein and J. Conway, J. Chem. Phys. 67, 1620 (1977).
2. J. Conway, J.C. Krupa, P. Delamoye and M. Genet, J. Chem. Phys. 74, 849 (1981).
3. J.C. Krupa, M. Hussonnois, M. Genet and R. Guillaumont, J. Chem. Phys. 77, 154 (1982).
4. R.W.M. D'Eye, J. Chem. Soc. 1950, 2764.
5. P. Chiotti, J.E. Fuller, C.H. Dock and M.C. Jha, J. Less Common Metals 31, 365 (1973).
6. J.T. Mason, M.C. Jha and P. Chiotti, J. Less Common Metals 34, 143 (1974).
7. S. Hubert, P. Delamoye, S. Lefrant, M. Lepostollec and M. Hussonnois, J. Solid State Chem. 36, 36 (1981).
8. C. Khan Malek, A. Péneau, L. Guibé, P. Delamoye and M. Hussonnois, J. Molecular Structure (in press).
9. L. Bernard, R. Currat, P. Delamoye, C. Zeyen, S. Hubert and R. de Kouchkovsky, J. of Physics C (in press).
10. P. Delamoye and R. Currat, J. de Phys. Lettres (in press).
11. M. Hussonnois, J.C. Krupa, M. Genet, L. Brillard and R. Carlier, J. Cryst. Growth 51, 11 (1981).
12. C. Daul, C.W. Schläpfer, B. Mohos, J. Ammeter and E. Gamp, Comp. Phys. Commun. 21, 385 (1981).
13. J.D. Axe, H.J. Stapleton and C.D. Jeffries, Phys. Rev. 121, 1630 (1961).

14. The crystal field parameters as used in this work and in ref. 3 are defined by B.G. Wybourne "Spectroscopic Properties of the Rare Earths", Wiley, New York (1965).
15. P. Delamoye, C. Khan Malek, S. Hubert, J.C. Krupa, M. Genet and R. Guillaumont. Proceedings of the "11 emes Journees des Actinides", Instituto di Chimica et Tecnologia dei Radioelementi, Padova G. Bombieri, et al. Editors (1981).
16. H.D. Amberger, W. Grape, and E. Stumpp, Actinides 1981, Asilomar Conference Abstracts, LBL 12441, N. Edelstein, Editor (1981).

Figure Captions

Figure 1. Absorption spectrum for $\text{Pa}^{4+}:\text{ThCl}_4$.

Figure 2. Absorption spectrum for $\text{Pa}^{4+}:\text{ThBr}_4$.

Figure 3. Influence of the incommensurate structure of ThBr_4 on the Pa^{4+} absorption band shapes at 4.2K. The shaded peak is typical.

Figure 4. Energy level diagram for $\text{Pa}^{4+}:\text{ThBr}_4$ and $\text{Pa}^{4+}:\text{ThCl}_4$.

Figure 5. A. Experimental EPR spectrum for $\text{Pa}^{4+}:\text{ThBr}_4$.

B. Calculated EPR spectrum for $\text{Pa}^{4+}:\text{ThBr}_4$.

Figure 6. A. Experimental EPR spectrum for $\text{Pa}^{4+}:\text{ThCl}_4$.

B. Calculated EPR spectrum for $\text{Pa}^{4+}:\text{ThCl}_4$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

XBL 8212-12044

Figure 6

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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