Lawrence Berkeley National Laboratory
Recent Work

Title
The EPR[Electron Paramagnetic Resonance] of Pu\(^{3+}\) and Cf\(^{3+}\) in Single Crystals of LuPO\(_4\)

Permalink
https://escholarship.org/uc/item/5wk21592

Journal
Physical Review B, 47(6)

Authors
Kot, W.K.
Edelstein, Norman M.
Abraham, M.M.
et al.

Publication Date
1992-07-01
Submitted to Physical Review B

The EPR of \( \text{Pu}^{3+} \) and \( \text{Cf}^{3+} \) in Single Crystals of \( \text{LuPO}_4 \)

W.K. Kot, N.M. Edelstein, M.M. Abraham, and L.A. Boatner

July 1992
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.
THE EPR OF Pu$^{3+}$ AND Cf$^{3+}$ IN SINGLE CRYSTALS OF LuPO$_4$

W.K. Kot and N.M. Edelstein
Chemical Sciences Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

and

M.M. Abraham and L.A. Boatner
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831-6056

This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and 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 EPR OF Pu$^{3+}$ AND Cf$^{3+}$ IN SINGLE CRYSTALS OF LuPO$_4$

W. K. Kot and N. M. Edelstein  
Chemical Sciences Division  
Lawrence Berkeley Laboratory, University of California  
Berkeley, California 94720

and

M. M. Abraham and L. A. Boatner  
Solid State Division, Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37831-6056

ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy has been used to investigate the ground-state properties of the actinide ions Pu$^{3+}$ ($5f^5$) and Cf$^{3+}$ ($5f^9$) incorporated as dilute impurities in single crystals of the tetragonal-symmetry host LuPO$_4$. The g-values of the electronic ground states were determined experimentally at a sample temperature of 4 K. These values are compared to those calculated using the free-ion parameters available from previous crystal-field analyses of Pu$^{3+}$ and Cf$^{3+}$ ions diluted in LaCl$_3$ host single crystals and a set of "crystal-field" parameters reported earlier for Cm$^{3+}$ ($5f^7$) ions in LuPO$_4$. These crystal-field parameters were obtained from spin-Hamiltonian parameters using operator-equivalent factors and the assumption that the zero-field splitting of the ground state of the $5f^7$ ion is due primarily to intermediate-coupling effects. The relatively poor agreement between the experimental and calculated g-values indicates that the crystal-field parameters obtained for Cm$^{3+}$ in LuPO$_4$ cannot be used to predict the correct electronic ground-state properties of the other actinide ions Pu$^{3+}$ and Cf$^{3+}$ in the identical host single crystal LuPO$_4$. Accordingly, in the case of actinide impurity ions in
single crystals, there is no simple correspondence between the spin-Hamiltonian parameters and the crystal-field parameters.
The electron paramagnetic resonance spectrum of the ion Pu$^{3+}$ (5f$^{5}$-electronic configuration) in the form of a dilute impurity has been investigated previously for a number of host single crystals. For most of the host crystals employed in these previous studies, the symmetry properties were such that the local crystal-field environment of the Pu$^{3+}$ ion was characterized by cubic symmetry. The cumulative results emerging from these previous spectroscopic investigations, have established that, in contrast to the case of the 4f lanthanide ions, for the 5f actinide ions, intermediate-coupling effects play an important role in determining the properties of the electronic energy levels. In particular, in the case of Pu$^{3+}$, the $J = 5/2$ manifold ground state was found to contain only 66% of the pure $^6H_{5/2}$ state with the remainder of the wave function consisting of other $J = 5/2$ states admixed by intermediate-coupling effects. In the present work, the tetragonal-symmetry single crystal LuPO$_4$ has been employed as a host material in order to investigate the effects of lower-symmetry crystal fields on the electronic properties of the intermediate-coupled $J = 5/2$ ground state of Pu$^{3+}$. For the case of Pu$^{3+}$ occupying a substitutional site in LuPO$_4$, the actinide ion is subjected to a crystalline electric field with D$_{2d}$ point-group symmetry - in contrast to the cubic-symmetry crystal fields characteristic of most previous EPR investigations of this ion. The Pu$^{3+}$-doped tetragonal single crystals of LuPO$_4$ employed in the present spectroscopic studies were grown in a glove-box-contained, platinum-wound furnace using a flux technique. In this growth process, a platinum crucible containing 6 g of PbHPO$_4$, 350 mg of Lu$_2$O$_3$, and 10 mg of PuO$_2$ was heated to 1360 °C in order to react the components to form the desired phosphate phases - including the Pb$_2$P$_2$O$_7$ phase which serves as a flux for the high-temperature solution-growth process. Following the high-temperature reaction period of a few hours, the crucible was cooled at 1°C/h from 1360 to 900°C and then cooled more quickly to room temperature. The Pu$^{3+}$-doped single crystals of LuPO$_4$
were subsequently removed from the entraining lead pyrophosphate by dissolving this flux material in boiling nitric acid for approximately three weeks. The even-even isotope $^{242}\text{Pu}$ was used as the actinide dopant in order to minimize radiation damage effects in the LuPO$_4$ host single crystal.

The electron paramagnetic resonance spectrum of Pu$^{3+}$ was observed using an X-band spectrometer operating at $\sim$9.2 GHz with the sample cooled to a temperature of $\sim$4 K. The observed EPR spectrum is associated with an effective $S = 1/2$ ground doublet of the Pu$^{3+}$ ground-state manifold. As shown in Figure 1, the experimentally determined angular variation of the EPR magnetic-dipole transition exhibited the tetragonal $D_{2d}$ symmetry characteristic of the substitutional lutetium host site. The Pu$^{3+}$ ground-state g-values of $g_|| = 0.772(2)$ and $g_\perp = 0.658(2)$ were determined from a least-squares fit, the results of which are also illustrated in Fig. 1A. There are presently no "crystal field" parameters available from the results of an optical analysis of Pu$^{3+}$ in LuPO$_4$. Accordingly, an approach was employed in which the crystal-field parameters determined previously for Cm$^{3+}$ in LuPO$_4$ were used to predict the properties of the ground electronic state for the neighboring actinide Pu$^{3+}$ ion. Assuming that the known large intermediate coupling effect is the dominant factor in producing the zero-field splitting of the ground state of the 5f$^7$ Cm$^{3+}$ ion in LuPO$_4$, the experimentally determined spin Hamiltonian parameters can be related to the crystal-field parameters through the use of operator equivalent factors. The resulting crystal-field parameters can then be applied to the calculation of wave functions of the crystal-field states of neighboring actinide ions occupying substitutional sites in the LuPO$_4$ host. This approach obviously relies on the basic assumption that the crystal-field parameters of the neighboring elements do not exhibit large variations in going from one element to another.
Using the previously determined crystal-field parameters for Cm$^{3+}$ in LuPO$_4$ and the free-ion spectroscopic parameters determined for Pu$^{3+}$ in LaCl$_3$\footnote{\textsuperscript{5}}, the ground state for Pu$^{3+}$ incorporated into the LuPO$_4$ host is calculated to be essentially a pure $|\pm 1/2\rangle$ state with little crystal-field-induced J-mixing. The corresponding calculated g-values are: $g_{||} = 0.4892$ and $g_{\perp} = 1.196$. Additionally, the first excited state is calculated to be another doublet at 45 cm$^{-1}$ with g-values of: $g_{||} = 1.203$ and $g_{\perp} = 0.1477$. There is obviously a serious discrepancy between these g-values, which were computed on the basis of the previously noted assumptions, and the actual experimentally determined g-values. This result clearly indicates that the assumed set of crystal-field parameters for Pu$^{3+}$ in LuPO$_4$ are not adequate to account for the experimental observations and that a set of parameters must be utilized that has been independently determined for the specific case of Pu$^{3+}$ in this host crystal.

The 5f$^9$ ion Cf$^{3+}$, which has been the subject of only one previous EPR study,\footnote{\textsuperscript{6}} represents the complementary electronic configuration to the Pu$^{3+}$ (5f$^5$) ion in the 5f transition series. In the only other reported EPR observation of Cf$^{3+}$, the spectrum of a polycrystalline powder of Cf$^{3+}$ in the compound Cs$_2$NaLuCl$_6$ was observed at a sample temperature of 4 K and a microwave frequency of $\sim$35 GHz.\footnote{\textsuperscript{6}} The trivalent Cf ion occupied a cubic-symmetry site in this chloride host, and the EPR spectrum exhibited a ten-line hyperfine structure, thereby confirming the nuclear spin of $^{249}$Cf as $9/2$. For pure Russell-Saunders coupling, the ground state of the 5f$^9$ ion would be $^6H_{15/2}$, and the observed ground state for Cf$^{3+}$ in Cs$_2$NaLuCl$_6$ was determined to be a $^6\Gamma_6$ doublet with a g value of 6.273.

In the present study of Cf$^{3+}$, host single crystals of LuPO$_4$ were grown using the procedure described above, and the $^{249}$Cf dopant was added to the starting composition in the form of 5 mg of the nitrate. The $^{249}$ Cf$^{3+}$ EPR spectrum was observed at a microwave frequency of $\sim$ 9.2 GHz and at a sample
temperature of 4 K. The Cf hyperfine structure was only partially resolved at this EPR frequency, and the peak-to-peak line width was found to be ~300 Gauss. The tetragonal angular variation associated with an effective $S = 1/2$ doublet is illustrated in Fig. 1B and was consistent with Cf$^{3+}$ occupying a substitutional Lu site in the LuPO$_4$ host. A least squares fit to the observed positions of the transitions as a function of the orientation of the applied magnetic field relative to the crystallographic axes of the host was made as shown in Fig. 1B resulting in the determination of the experimental g-values of $g_{||} = 3.56(2)$ and $g_{\perp} = 7.79(3)$.

The Cf$^{3+}$ ground state that was calculated based on the previously determined crystal parameters of Cm$^{3+}$ in LuPO$_4$ was found to be a $\Gamma_7$ doublet with a wave function given by:

$$-0.943 |\pm 15/2> + 0.303 |\pm 7/2> (+ \text{smaller terms})$$

which, using a $g_J$ value of 1.279, yields a calculated $g_{||}$ value of 17.89 and $g_{\perp} = 0$.

An excited $\Gamma_6$ state was calculated to lie at an energy of 78 cm$^{-1}$ above the ground state with $g_{||} = 4.144$ and $g_{\perp} = 8.242$. The ground J = 15/2 manifold of Cf$^{3+}$ will split into 8 doublets in $D_{2d}$ symmetry, and it is conceivable that a slight variation in the crystal field could produce a different ground state. As was found for the case of Pu$^{3+}$ in LuPO$_4$, however, it is clear that the ground state of Cf$^{3+}$ in this host cannot be predicted in a straightforward manner by employing crystal field parameters determined for a neighboring actinide ion substituting in the same host crystal.

This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S.D.O.E.
under Contract No. DE-AC03-76SF00098. The authors are indebted to John Bigelow and other staff members of the transplutonium element production facilities at the Oak Ridge National Laboratory. The authors also acknowledge with thanks the excellent technical contributions of H.E. Harmon and C. B. Finch.
References


Figure Captions

Figure 1. Experimental EPR measurements as a function of the angle between the crystallographic c axis and the magnetic field. The solid curves represent a least-squares fit of the data to the expression $g^2 = g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$.

A) Pu$^{3+}$/LuPO$_4$, microwave frequency = 9.223 GHz, $g_{||} = 0.772(2)$, and $g_{\perp} = 0.658(2)$. B) Cf$^3$/LuPO$_4$, microwave frequency = 9.217 GHz, $g_{||} = 3.56(2)$ and $g_{\perp} = 7.79(3)$. 
Pu$^{3+}$ / LuPO$_4$ EPR

Cf$^{3+}$ / LuPO$_4$ EPR

Figure 1