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The EPR[Electron Paramagnetic Resonance] of Pu<sup>3+</sup> and Cf<sup>3+</sup> in Single Crystals of LuPO<sub>4</sub>

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### Authors

Kot, W.K.  
Edelstein, Norman M.  
Abraham, M.M.  
[et al.](#)

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

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THE EPR OF  $\text{Pu}^{3+}$  AND  $\text{Cf}^{3+}$  IN SINGLE CRYSTALS OF  $\text{LuPO}_4$

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

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# THE EPR OF $\text{Pu}^{3+}$ AND $\text{Cf}^{3+}$ IN SINGLE CRYSTALS OF $\text{LuPO}_4$

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  $\text{Pu}^{3+}$  ( $5f^5$ ) and  $\text{Cf}^{3+}$  ( $5f^9$ ) incorporated as dilute impurities in single crystals of the tetragonal-symmetry host  $\text{LuPO}_4$ . 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  $\text{Pu}^{3+}$  and  $\text{Cf}^{3+}$  ions diluted in  $\text{LaCl}_3$  host single crystals and a set of "crystal-field" parameters reported earlier for  $\text{Cm}^{3+}$  ( $5f^7$ ) ions in  $\text{LuPO}_4$ . 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  $\text{Cm}^{3+}$  in  $\text{LuPO}_4$  cannot be used to predict the correct electronic ground-state properties of the other actinide ions  $\text{Pu}^{3+}$  and  $\text{Cf}^{3+}$  in the identical host single crystal  $\text{LuPO}_4$ . 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  $\text{Pu}^{3+}$  ( $5f^5$ -electronic configuration) in the form of a dilute impurity has been investigated previously for a number of host single crystals. <sup>(1)</sup> For most of the host crystals employed in these previous studies, the symmetry properties were such that the local crystal-field environment of the  $\text{Pu}^{3+}$  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  $\text{Pu}^{3+}$ , the  $J = 5/2$  manifold ground state was found to contain only 66% of the pure  ${}^6\text{H}_{5/2}$  state with the remainder of the wave function consisting of other  $J = 5/2$  states admixed by intermediate-coupling effects.<sup>(2)</sup> In the present work, the tetragonal-symmetry single crystal  $\text{LuPO}_4$  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  $\text{Pu}^{3+}$ . For the case of  $\text{Pu}^{3+}$  occupying a substitutional site in  $\text{LuPO}_4$ , 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  $\text{Pu}^{3+}$ -doped tetragonal single crystals of  $\text{LuPO}_4$  employed in the present spectroscopic studies were grown in a glove-box-contained, platinum-wound furnace using a flux technique.<sup>(3)</sup> In this growth process, a platinum crucible containing 6 g of  $\text{PbHPO}_4$ , 350 mg of  $\text{Lu}_2\text{O}_3$ , and 10 mg of  $\text{PuO}_2$  was heated to  $1360^\circ\text{C}$  in order to react the components to form the desired phosphate phases - including the  $\text{Pb}_2\text{P}_2\text{O}_7$  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  $1^\circ\text{C}/\text{h}$  from  $1360$  to  $900^\circ\text{C}$  and then cooled more quickly to room temperature. The  $\text{Pu}^{3+}$ -doped single crystals of  $\text{LuPO}_4$

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  $\text{LuPO}_4$  host single crystal.

The electron paramagnetic resonance spectrum of  $\text{Pu}^{3+}$  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  $\text{Pu}^{3+}$  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  $\text{Pu}^{3+}$  ground-state  $g$ -values of  $g_{\parallel} = 0.772(2)$  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  $\text{Pu}^{3+}$  in  $\text{LuPO}_4$ . Accordingly, an approach was employed in which the crystal-field parameters determined previously for  $\text{Cm}^{3+}$  in  $\text{LuPO}_4$ <sup>(4)</sup> were used to predict the properties of the ground electronic state for the neighboring actinide  $\text{Pu}^{3+}$  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  $5f^7$   $\text{Cm}^{3+}$  ion in  $\text{LuPO}_4$ , 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  $\text{LuPO}_4$  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  $\text{Ce}^{3+}$  in  $\text{LuPO}_4$  and the free-ion spectroscopic parameters determined for  $\text{Pu}^{3+}$  in  $\text{LaCl}_3$ <sup>(5)</sup>, the ground state for  $\text{Pu}^{3+}$  incorporated into the  $\text{LuPO}_4$  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:  $g_{\parallel} = 0.4892$  and  $g_{\perp} = 1.196$ . Additionally, the first excited state is calculated to be another doublet at  $45 \text{ cm}^{-1}$  with g-values of:  $g_{\parallel} = 1.203$  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  $\text{Pu}^{3+}$  in  $\text{LuPO}_4$  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  $\text{Pu}^{3+}$  in this host crystal.

The  $5f^9$  ion  $\text{Cf}^{3+}$ , which has been the subject of only one previous EPR study,<sup>(6)</sup> represents the complementary electronic configuration to the  $\text{Pu}^{3+}$  ( $5f^5$ ) ion in the 5f transition series. In the only other reported EPR observation of  $\text{Cf}^{3+}$ , the spectrum of a polycrystalline powder of  $\text{Cf}^{3+}$  in the compound  $\text{Cs}_2\text{NaLuCl}_6$  was observed at a sample temperature of 4 K and a microwave frequency of  $\sim 35 \text{ GHz}$ .<sup>(6)</sup> 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  $^{249}\text{Cf}$  as  $9/2$ . For pure Russell-Saunders coupling, the ground state of the  $5f^9$  ion would be  $^6\text{H}_{15/2}$ , and the observed ground state for  $\text{Cf}^{3+}$  in  $\text{Cs}_2\text{NaLuCl}_6$  was determined to be a  $\Gamma_6$  doublet with a g value of 6.273.

In the present study of  $\text{Cf}^{3+}$ , host single crystals of  $\text{LuPO}_4$  were grown using the procedure described above, and the  $^{249}\text{Cf}$  dopant was added to the starting composition in the form of 5 mg of the nitrate. The  $^{249}\text{Cf}^{3+}$  EPR spectrum was observed at a microwave frequency of  $\sim 9.2 \text{ GHz}$  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  $\text{Cf}^{3+}$  occupying a substitutional Lu site in the  $\text{LuPO}_4$  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  $g_{\parallel} = 3.56(2)$  and  $g_{\perp} = 7.79(3)$ .

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

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

which, using a  $g_J$  value of 1.279, yields a calculated  $g_{\parallel}$  value of 17.89 and  $g_{\perp} = 0$ . An excited  $\Gamma_6$  state was calculated to lie at an energy of  $78 \text{ cm}^{-1}$  above the ground state with  $g_{\parallel} = 4.144$  and  $g_{\perp} = 8.242$ . The ground  $J = 15/2$  manifold of  $\text{Cf}^{3+}$  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  $\text{Pu}^{3+}$  in  $\text{LuPO}_4$ , however, it is clear that the ground state of  $\text{Cf}^{3+}$  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.

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## References

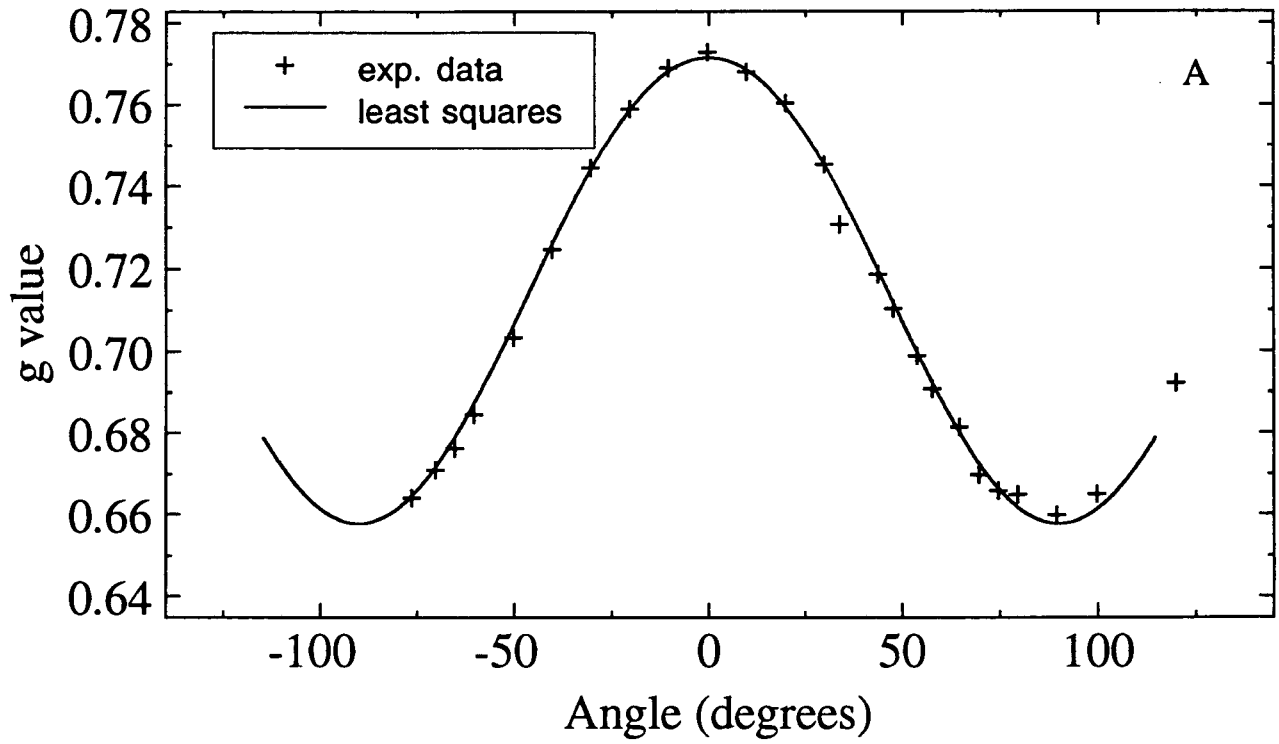
- (1) L. A. Boatner and M. M. Abraham, *Reports on Progress in Physics* **41**, 87 (1978).
- (2) N. Edelstein, H. F. Mollet, W. C. Easley, and R. J. Mehlhorn, *J. Chem. Phys.* **51**, 3281 (1969).
- (3) M. M. Abraham, L. A. Boatner, and J. O. Ramey, *J. Chem. Phys.* **83**, 2754 (1985).
- (4) W. K. Kot, Ph. D. Thesis, University of California, Berkeley (1991);  
W. K. Kot, N. Edelstein, M. M. Abraham, and L. A. Boatner, to be published.
- (5) W. T. Carnall, Argonne National Laboratory, ANL-890/39 (1989).
- (6) N. Edelstein and D. G. Karraker, *J. Chem. Phys.* **62**, 938 (1975).

## 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  $g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$ .

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

# $\text{Pu}^{3+} / \text{LuPO}_4$ EPR



# $\text{Cf}^{3+} / \text{LuPO}_4$ EPR

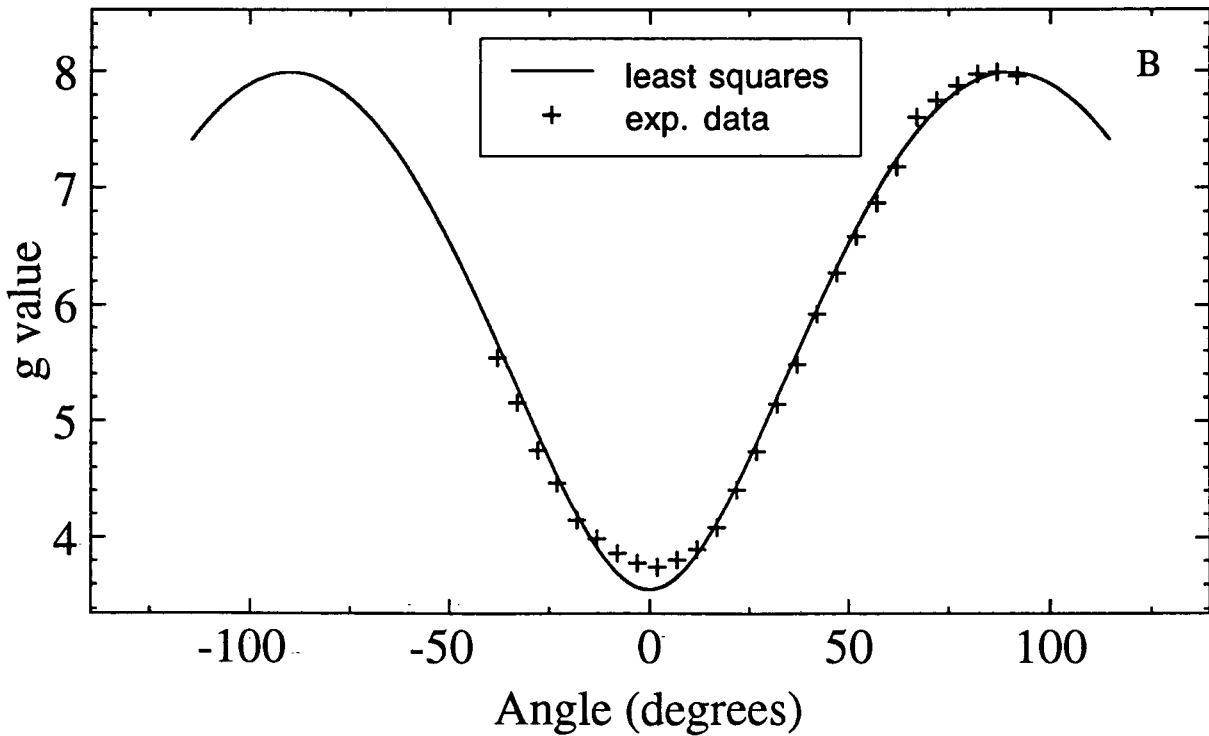


Figure 1

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