

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

CRYSTAL FIELD ANALYSIS OF Tm<sup>3+</sup> AND Yb<sup>3+</sup> IN YPO<sub>4</sub> AND LuPO<sub>4</sub>

### Permalink

<https://escholarship.org/uc/item/6t36h2dt>

### Author

Becker, P.C.

### Publication Date

1984-04-01

**Lawrence Berkeley Laboratory**  
UNIVERSITY OF CALIFORNIA

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

MAY 30 1984

LIBRARY AND  
DOCUMENTS SECTION

**Materials & Molecular  
Research Division**

Submitted to the Journal of Chemical Physics

CRYSTAL FIELD ANALYSIS OF  $Tm^{3+}$  AND  $Yb^{3+}$  IN  
 $YPO_4$  AND  $LuPO_4$

P.C. Becker, T. Hayhurst, G. Shalimoff, J.G. Conway,  
N. Edelstein, L.A. Boatner, and M.M. Abraham

April 1984

**For Reference**  
Not to be taken from this room



LBL-17443  
c.1

## **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.

Crystal Field Analysis of  $Tm^{3+}$  and  $Yb^{3+}$   
in  $YPO_4$  and  $LuPO_4$

P. C. Becker, T. Hayhurst,<sup>†</sup> G. Shalimoff, J.G. Conway, and N. Edelstein  
Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
and  
Department of Physics  
University of California  
Berkeley, California 94720

L.A. Boatner and M.M. Abraham  
Solid State Division  
Oak Ridge National Laboratory\*  
Oak Ridge, Tennessee 37830.

Abstract

The optical and near infrared absorption of dilute  $Tm^{3+}$  and  $Yb^{3+}$  impurities in  $YPO_4$  and  $LuPO_4$  single crystals have been measured at liquid helium and nitrogen temperatures. For  $Tm^{3+}$ , the spectral region from 5000 to 38,000  $cm^{-1}$  was examined and Zeeman spectra were obtained in the visible region. The observed transitions were assigned and fit to a semiempirical Hamiltonian with adjustable parameters via a least-squares procedure. Satisfactory fits and good agreement between the calculated and measured g values were obtained.

For  $Yb^{3+}$ , there are more parameters than experimental levels, so  $\zeta$ ,  $B_0^2$ ,  $B_0^4$ , and  $B_4^4$  were adjusted, while  $B_0^6$  and  $B_4^6$  were fixed at the values found for  $Tm^{3+}$ . Energy levels and Zeeman splittings calculated with these parameters are in good agreement with the measured quantities.

<sup>†</sup> Permanent address: The Aerospace Corporation, PO Box 92957/M2-251, Los Angeles, CA 90009.

\* Operated by Union Carbide for the U.S. Department of Energy under contract W-7405-eng-26.

## I. Introduction:

The present study of the optical spectra of thulium and ytterbium in  $\text{YPO}_4$  and  $\text{LuPO}_4$  represents a continuation of previous investigations of the chemical and physical properties of rare-earth impurity ions in lanthanide orthophosphates.<sup>1-7</sup> The lanthanide orthophosphates in the form of polycrystalline ceramic bodies represent a promising new class of materials for use as a primary containment medium for the long term disposal of high level nuclear wastes.<sup>8-10</sup> The solid state chemical properties of orthophosphates formed by mixed lanthanides are of particular interest since a relatively high concentration (> 30 wt. %) of various lanthanides is present in the waste resulting from reprocessing of light water reactor spent fuel.

The pure lanthanide orthophosphates are structurally divided into two classes: the first half of the series ( $\text{LaPO}_4$  to  $\text{GdPO}_4$ ) has the monoclinic "monazite structure" (space group  $P2_1/n$ ), while the second half of the series ( $\text{TbPO}_4$  to  $\text{LuPO}_4$ , plus  $\text{YPO}_4$  and  $\text{ScPO}_4$ ) is characterized by the tetragonal zircon structure (space group  $I4_1/amd$ ). Previous investigations of the solid state chemical properties of both structural types have included determinations of the site symmetries and valence states of both iron group and rare earth impurities by means of electron paramagnetic (EPR) spectroscopy.<sup>1-3,11</sup> Additional studies of both doped and pure lanthanide orthophosphates have included x-ray diffraction structural refinements,<sup>12,13,14</sup> Raman investigations,<sup>15</sup> and previous optical absorption experiments on  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$  diluted in  $\text{LuPO}_4$  and  $\text{YPO}_4$ .<sup>6,7</sup> Knoll has previously reported and

assigned the visible absorption spectrum of  $\text{Tm}^{3+}$  diluted in  $\text{YPO}_4$ .<sup>17</sup>

In the present work optical absorption and Zeeman effect studies have been performed that complement the earlier investigations. Trivalent thulium and ytterbium were incorporated as dilute impurities in  $\text{YPO}_4$  and  $\text{LuPO}_4$  where they occupy substitutional sites with local  $D_{2d}$  symmetry. Energy levels corresponding to the irreducible representations of the  $D_{2d}$  point group were derived from the free ion  $f^{12}$  configuration for  $\text{Tm}^{3+}$  and the free ion  $f^{13}$  configuration for  $\text{Yb}^{3+}$ .

Parameters describing the electrostatic, spin orbit, and crystal-field interactions were adjusted using a least-squares minimization procedure in order to obtain a fit to a semiempirical Hamiltonian. The calculations were made using a full diagonalization of the Hamiltonian matrix in the  $(L, S, J, J_z)$  representation. Good agreement was obtained between the observed and calculated energies and g values. The Zeeman pattern for  $\text{Yb}^{3+}$  in  $\text{YPO}_4$  was analyzed in detail since the accidental degeneracy of two of the excited states results in a mixing of these states when an applied magnetic field is not parallel to the  $S_4$  axis.

## II. Experimental Procedure:

The  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  doped crystals employed in this work were grown by means of a flux technique that has been described elsewhere.<sup>8,16</sup> Thulium and ytterbium doping levels of approximately 0.1 wt.% were employed.

In the case of  $\text{Tm}^{3+}$  in  $\text{YPO}_4$ , the spectra from 250 to 1700 nm ( $40,000$  to  $5800 \text{ cm}^{-1}$ ) were measured using a Cary Model 17 spectrophotometer with sample temperatures of 2 and 77 K. Linear

polarization of the spectra was obtained in the directions perpendicular and parallel to the crystal axis. These transitions supplement previously reported photographic measurements.<sup>17</sup>

For  $\text{Tm}^{3+}$  in  $\text{LuPO}_4$  a similar procedure was employed. The  ${}^3\text{F}_4$  and  ${}^3\text{H}_5$  lines were scanned at approximately 2K and 77K in the IR region. Photographic observations were made between 12,000 and 38,000  $\text{cm}^{-1}$  on a 3.4 m Ebert spectrograph with a reciprocal dispersion of about 5.2  $\text{\AA}/\text{mm}$  in the first order. Linear polarization of the spectra was obtained in the directions perpendicular and parallel to the crystal axis. All spectra were photographed at both liquid He and  $\text{N}_2$  temperatures and Zeeman splittings were recorded with the crystal in a magnetic field of 26.9 kG. No splittings were observed with the c axis perpendicular to the applied magnetic field.

In the case of  $\text{Yb}^{3+}$  in  $\text{YPO}_4$  and  $\text{LuPO}_4$ , scans were made at both pumped liquid He and  $\text{N}_2$  temperatures from 9,000 to 11,000  $\text{cm}^{-1}$ . Linear polarization of the spectra was obtained in the directions perpendicular and parallel to the crystal axis. The experimental g values for the ground state doublets were determined by means of EPR spectroscopy and have been reported previously.<sup>1</sup> Zeeman splittings in the 10,000  $\text{cm}^{-1}$  region were photographed at liquid He temperatures with the crystallographic c axis both parallel and perpendicular to the magnetic field of 26.9 kG.

### III. Analysis and Discussion:

The energy levels within an  $f^n$  configuration in  $D_{2d}$  symmetry can be written in terms of the atomic free ion ( $H_{FI}$ ) and crystal field

( $H_{CF}$ ) Hamiltonians as follows:<sup>18,19</sup>

$$H_{FI} = \sum_{k=0,2,4,6} F^k(nf,nf) f_k + \zeta_f a_{so} + \alpha L(L+1) \\ + \beta G(G_2) + \gamma (R_7) + \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k$$

and

$$H_{CF} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 (C_4^4 + C_{-4}^4) + B_0^6 C_0^6 \\ + B_4^6 (C_4^6 + C_{-4}^6)$$

The  $F^k(nf,nf)$ 's and  $\zeta_f$  represent, respectively, the radial parts of the electrostatic and spin orbit interactions between  $f$  electrons, while  $f_k$  and  $a_{so}$  are the angular parts of the interactions.  $\alpha$ ,  $\beta$ , and  $\gamma$  are the parameters associated with the two-body effective operators of configuration interaction. The  $M^k$  parameters represent the spin-spin and spin-other-orbit interactions while the  $P^k$  parameters arise from electrostatic-spin-orbit interactions with higher configurations. The crystal field interaction for  $D_{2d}$  symmetry is parameterized by  $B_0^2$ ,  $B_0^4$ ,  $B_4^4$ ,  $B_0^6$ , and  $B_4^6$ ; and the angular operators,  $C_q^{(k)}$ , are the usual Racah tensors.<sup>18</sup>

### IIIa. Absorption Spectra and Zeeman Effect of the Thullium Ion

$Tm^{3+}$  has an  $f^{12}$  configuration. The crystal field eigenstates carry the  $\Gamma_1$  through  $\Gamma_5$  point group representations associated with the  $D_{2d}$  site symmetry. Selection rules for the allowed



electric dipole transitions are identical to those for  $\text{Pr}^{3+}$ .<sup>7</sup>

The  $\Gamma_5$  representation is two dimensional and the corresponding levels can exhibit splitting under an applied external magnetic field parallel to the crystal axis. The observed  $\text{Tm}^{3+}$  spectra are well characterized by their group theoretical selection rules, and the  $D_{2d}$  symmetry sites of  $\text{Tm}^{3+}$  in the  $\text{YPO}_4$  and  $\text{LuPO}_4$  hosts are so similar that the wavelengths and relative intensities of the optical transitions are nearly identical in each crystal. The observed and calculated values of the energy levels and g values for  $\text{Tm}^{3+}$  are given in Table 1 along with the eigenvector composition and irreducible representations. Table 3 presents a listing of the atomic and crystal field parameters obtained from the analysis outlined previously.

Thirty-seven experimental eigenvalues were assigned for  $\text{Tm}^{3+}$  in  $\text{YPO}_4$ , and 35 experimental eigenvalues and four g values were assigned for  $\text{Tm}^{3+}$  in  $\text{LuPO}_4$ . Data for the low lying excited states were obtained from measurements made with the samples at liquid nitrogen temperature. The Zeeman spectra proved to be particularly useful in identifying the  $\Gamma_5$  lines. The fits obtained for  $\text{Tm}^{3+}$  in  $\text{YPO}_4$  and  $\text{LuPO}_4$  were characterized by reduced rms energy deviations of  $13.6 \text{ cm}^{-1}$  and  $10.0 \text{ cm}^{-1}$ , respectively. In the case of  $\text{LuPO}_4$ , the g value agreements were quite good.

The level assignments reported previously for  $\text{Tm}^{3+}$  in  $\text{YPO}_4$ <sup>17</sup> were changed to agree with the present experimental results. In Table II of reference 17, the multiplet listed as  $^3F_4$  was corrected to

${}^3H_4$ . The line listed at  $21260.15 \text{ cm}^{-1}$  was not used in our analysis since the  ${}^1G_4$  multiplet contains only one level of  $\Gamma_4$  symmetry, which was selected to be the line at  $21291.88 \text{ cm}^{-1}$ . Two levels presented in that table differed substantially from the values we observed. We retained our experimental values for the purpose of the crystal field fit, namely  $14467.18 \text{ cm}^{-1}$  was replaced by  $14451.0 \text{ cm}^{-1}$  and  $14453.98 \text{ cm}^{-1}$  was replaced by  $14439.0 \text{ cm}^{-1}$ .  $\text{Tm}^{3+}$  in  $\text{YPO}_4$  has several unassigned lines at liquid helium temperature,  $14424 \text{ cm}^{-1}$ ,  $15085 \text{ cm}^{-1}$ , and  $21262 \text{ cm}^{-1}$ ; their intensities relative to the assigned lines do not change from liquid helium to liquid nitrogen temperatures implying that they are not transitions from low lying excited states.  $\text{Tm}^{3+}$  in  $\text{LuPO}_4$  has similar unassigned lines at  $5796 \text{ cm}^{-1}$ ,  $21239 \text{ cm}^{-1}$ , and  $21326 \text{ cm}^{-1}$ . These lines could arise from magnetic dipole transitions, but we have not included them in our analysis. It is interesting to note that the low lying crystal field levels obtained for  $\text{Tm}^{3+}$  in  $\text{YPO}_4$  and  $\text{LuPO}_4$  agree well with the electronic Raman levels measured by Guha for pure  $\text{TmPO}_4$ .<sup>23</sup> However, we assign the level at  $84 \text{ cm}^{-1}$  to be of  $\Gamma_3$  symmetry.

#### II Ib. Absorption spectrum of the Ytterbium ion

$\text{Yb}^{3+}$  has an  $f^{13}$  configuration. The crystal field eigenstates carry the  $\Gamma_6$  and  $\Gamma_7$  representations associated with the  $D_{2d}$  symmetry group. The selection rules are identical to those for  $\text{Nd}^{3+}$ .<sup>7</sup>

For  $\text{Yb}^{3+}$  in  $\text{YPO}_4$  and  $\text{LuPO}_4$ , the small number of transitions allowed are insufficient to determine uniquely the crystal field and spin orbit parameters. The following procedure was employed. First, the corresponding parameters from  $\text{Tm}^{3+}$  were used to predict an energy level scheme that was fairly close to the experimentally observed levels, allowing their assignment. Four transitions having been thus selected, the spin orbit parameter and crystal field parameters  $B_0^2$ ,  $B_0^4$ , and  $B_4^4$  were adjusted to produce an energy level scheme that exactly reproduced the experimentally observed one. The resultant parameters were quite close to their corresponding values for  $\text{Tm}^{3+}$ . An additional feature was observed in both  $\text{YPO}_4$  and  $\text{LuPO}_4$  around  $10,600 \text{ cm}^{-1}$  consisting of a main peak with shoulders and sidebands. This feature does not correspond to any pure electronic transitions of  $\text{Yb}^{3+}$  as predicted by our model. Further tests of our crystal field model for  $\text{Yb}^{3+}$ , from the observed Zeeman patterns, are discussed in the next section. Listings of observed and calculated energies and g values are compiled in Table 2.

### IIIc. Zeeman study of the Ytterbium ion

Ground state g values are in excellent agreement with previously reported EPR measurements.<sup>1</sup> In the case of a magnetic field applied perpendicularly to the c axis, the Zeeman pattern of the excited states in the  $10,200 \text{ cm}^{-1}$  region were obtained. For  $\text{Yb}^{3+}$  in  $\text{LuPO}_4$ , the measured g values agree well with the calculated values. For  $\text{Yb}^{3+}$  in  $\text{YPO}_4$ , the situation is more complex. The  $\Gamma_6$  and

$\Gamma_7$  levels, situated respectively at  $10257.81 \text{ cm}^{-1}$  and  $10258.36 \text{ cm}^{-1}$  are so nearly degenerate that they will be substantially mixed by the magnetic field Hamiltonian. The g values displayed in the tables are computed assuming that there is no mixing between adjacent states, so that a more rigorous treatment is needed. The Zeeman Hamiltonian is calculated within the subspace spanned by the two levels and then diagonalized. The Zeeman operator for any angle  $\phi$  in the plane perpendicular to the c axis is:

$$\mathcal{H}_Z = \mu_B g H (L_x + 2S_x) \cos \phi + \mu_B g H (L_y + 2S_y) \sin \phi$$

where  $\phi$  is the angle between the x axis of the local  $D_{2d}$  symmetry site and the magnetic field. A phase factor  $e^{\pm i\phi}$  is thus introduced into the off diagonal matrix elements.<sup>21</sup> For our measurements in  $\text{Yb}^{3+}$  in  $\text{YPO}_4$  the magnetic field was oriented along a crystallographic axis which corresponds to  $\phi = 45^\circ$ . The calculated and experimentally observed transitions are given in Table 4 using the EPR values for the ground state splittings. The agreement is excellent.

Zeeman data were also measured with the magnetic field parallel to the c axis. In this case, however, not all the transitions allowed were observed due to selection rules and other unexplained reasons. Polarization data could not be obtained because of the long times needed to expose the photographic plates in this region. The data obtained are consistent with the calculated g values as given in Table 2.

#### IIIId. Discussion

The values of the crystal field parameters for  $\text{Ln}^{3+}/\text{YPO}_4$  crystals appear to be fairly consistent across the lanthanide series (see Table 5) with perhaps the early members of the series  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ , showing the largest deviations from the mean values. The data for  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$  have not been analyzed with the inclusion of higher order terms in the free ion Hamiltonian and the complete diagonalization of this Hamiltonian with the addition of the crystal field Hamiltonian.<sup>19</sup> Therefore the parameter values for these ions must be regarded as preliminary. The values of the  $B_4^6$  are rather small and have large uncertainties which result in inconsistent signs for this parameter across the series. These results are similar to those found for the much more complete sets of crystal field parameters of  $\text{Ln}^{3+}/\text{LaCl}_3$ .<sup>20</sup>

#### IV. Summary and conclusions

Investigations of the low temperature optical spectra of  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  impurities diluted in the zircon structure orthophosphates,  $\text{YPO}_4$  (xenotime) and  $\text{LuPO}_4$ , were carried out. The optical data for  $\text{Tm}^{3+}$  in the two hosts were used in making assignments to the free ion  $4f^{12}$  states, and these results were used in a least-squares fit to a semiempirical Hamiltonian. In the case of the  $4f^{13}$  configuration ion  $\text{Yb}^{3+}$  not all the parameters were fit, the ones not being adjusted being fixed to their corresponding value for  $\text{Tm}^{3+}$ . This yielded satisfactory fits to the experimental results, in particular

for the Zeeman pattern of the excited state. Calculated g values for the ground state were found to be in good agreement with those determined by using EPR spectroscopy.

#### Acknowledgements

This work was supported 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.

REFERENCES

1. M. M. Abraham, L. A. Boatner, J. O. Ramey, and M. Rappaz, J. Chem. Phys. 78, 3 (1983).
2. M. Rappaz, L. A. Boatner, and M. M. Abraham, J. Chem. Phys. 73, 1095 (1980).
3. M. Rappaz, M. M. Abraham, J. O. Ramey, and L. A. Boatner, Phys. Rev. B 23, 1012 (1981).
4. L. A. Boatner, M. M. Abraham, and M. Rappaz, Scientific Basis for Nuclear Waste Management, ed. by J. G. Moore (Plenum Press, New York, 1981), Vol. 3, p. 181.
5. M. M. Abraham, L. A. Boatner, and M. Rappaz, Nuclear and Electron Resonance Spectroscopies Applied to Materials Science, ed. by E. N. Kaufman and G. K. Shenoy (Elsevier North-Holland, New York, 1981), Vol. 3, p. 475.
6. T. Hayhurst, G. Shalimoff, N. Edelstein, L. A. Boatner, and M. M. Abraham, J. Chem. Phys. 74, 5449 (1981).
7. T. Hayhurst, G. Shalimoff, J. G. Conway, N. Edelstein, L. A. Boatner, and M. M. Abraham, J. Chem. Phys. 76, 3960 (1982).
8. L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, R. J. Floran, P. G. Huray, and M. Rappaz, in Management of Alpha-Contaminated Wastes, IAEA-SM-246/73 (IAEA, Vienna, Austria, 1981), p. 411.
9. L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, Scientific Basis for Nuclear Waste Management, ed. by C. J. Northrup (Plenum Press, New York, 1980)

- Vol. II, p. 289.
10. M. Petek, M. M. Abraham, and L. A. Boatner, Scientific Basis for Nuclear Waste Management, ed. by S. V. Topp (Elsevier North-Holland, New York, 1982), Vol. 4, p. 181.
  11. M. Rappaz, J. O. Ramey, L. A. Boatner, and M. M. Abraham, J. Chem. Phys. 76, 40 (1982).
  12. W. O. Milligan, D. F. Mullica, G. W. Beall, and L. A. Boatner, Inorg. Chimica Acta. 60, 39 (1982).
  13. W. O. Milligan, D. F. Mullica, G. W. Beall, and L. A. Boatner, J. Inorg. Nucl. Chem. (in press).
  14. W. O. Milligan, D. F. Mullica, G. W. Beall, and L. A. Boatner, Acta Cryst. (in press).
  15. G. M. Begun, G. W. Beall, L. A. Boatner, and W. T. Gregor, J. Raman Spectros. 11, 273 (1981).
  16. R. S. Feigelson, J. Am. Ceram. Soc. 47, 257 (1964).
  17. K. D. Knoll, Phys. Stat. Sol. (b) 45, 553 (1971).
  18. B. G. Wybourne, Spectroscopic Properties of the Rare Earths (Wiley, New York, 1965).
  19. 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).
  20. W. T. Carnall, H. Crosswhite, H. M. Crosswhite, Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in  $\text{LaF}_3$ , Argonne National Laboratory Report (1977).



21. T. Murao, F. H. Spedding, R. H. Good, Jr., J. Chem. Phys. 42, 993 (1965).
22. C. Brecher, H. Samelson, R. Riley, and A. Lempicki, J. Chem. Phys. 49, 3303 (1968).
23. S. Guah, Phys. Rev. B 23, 6790 (1981).
24. P.J. Becker, Phys. Stat. Sol. 38, 379 (1970).
25. C.A. Morrison and R.P. Leavitt, in "Handbook on the Physics and Chemistry of Rare Earths," K.A. Gschneider, L. Eyring, Ed., Vol. 5, 1982, pp. 461-692.

Table 1a

Observed and calculated energies and  
g values for  $Tm^{3+}$  in  $YPO_4$ .

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	largest	(2S+1)L(J,J <sub>z</sub> ) % second
$\Gamma_1$	0.0	0.0			77	3H(6,0)	23 3H(6,±4)
$\Gamma_5$	28.5	30.7	3.5		65	3H(6,-1)	23 3H(6,-5)
$\Gamma_3$	89.2	76.2			98	3H(6,±2)	
$\Gamma_5$	142.2	144.8	8.2		74	3H(6,-5)	14 3H(6,-1)
$\Gamma_2$	191.8				99	3H(6,±4)	
$\Gamma_1$	244.4				77	3H(6,±4)	23 3H(6,0)
$\Gamma_4$	253.5				86	3H(6,±2)	13 3H(6,±6)
$\Gamma_5$	272.7		-4.6		77	3H(6,3)	20 3H(6,-1)
$\Gamma_3$	330.4				98	3H(6,±6)	
$\Gamma_4$	337.6				86	3H(6,±6)	13 3H(6,±2)
$\Gamma_3$	5611.0				62	3F(4,±2)	30 1G(4,±2)
$\Gamma_5$	5702.5	5692.0	-1.5		37	3F(4,-1)	26 3F(4,3)
$\Gamma_1$	5712.7				51	3F(4,±4)	12 3F(4,0)
$\Gamma_2$	5743.7				64	3F(4,±4)	28 1G(4,±4)
$\Gamma_4$	5776.0	5774.0			63	3F(4,±2)	29 1G(4,±2)
$\Gamma_5$	5850.7	5850.0	-3.1		38	3F(4,3)	26 3F(4,-1)
$\Gamma_1$	5864.8				52	3F(4,0)	23 1G(4,0)
$\Gamma_2$	8229.7	8242.0			71	3H(5,0)	29 3H(5,±4)
$\Gamma_5$	8261.0	8264.0	0.1		72	3H(5,-1)	25 3H(5,3)

Tm<sup>3+</sup>:YPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	(2S+1)L(J,J <sub>z</sub> ) %	second
Γ <sub>4</sub>	8281.6	8282.0			100		3H(5,±2)
Γ <sub>1</sub>	8342.7	8357.0			100		3H(5,±4)
Γ <sub>2</sub>	8389.3	8395.0			71	29	3H(5,±4) 3H(5,0)
Γ <sub>5</sub>	8401.8	8397.0	-3.3		72	21	3H(5,3) 3H(5,-1)
Γ <sub>3</sub>	8418.5				100		3H(5,±2)
Γ <sub>5</sub>	8467.9	8470.0	9.3		91	6	3H(5,-5) 3H(5,-1)
Γ <sub>1</sub>	12543.1	12528.0			57	24	3H(4,0) 3F(4,0)
Γ <sub>5</sub>	12562.2	12551.8	-3.4		42	18	3H(4,3) 3F(4,3)
Γ <sub>5</sub>	12677.1	12662.5	-0.4		42	19	3H(4,-1) 3F(4,-1)
Γ <sub>3</sub>	12687.2				58	28	3H(4,±2) 3F(4,±2)
Γ <sub>2</sub>	12730.9				59	26	3H(4,±4) 3F(4,±4)
Γ <sub>1</sub>	12744.6				56	25	3H(4,±4) 3F(4,±4)
Γ <sub>4</sub>	12789.0	12780.8			59	27	3H(4,±2) 3F(4,±2)
Γ <sub>5</sub>	14405.9	14409.2	-5.2		85	15	3F(3,3) 3F(3,-1)
Γ <sub>5</sub>	14436.3	14439.0	0.9		85	15	3F(3,-1) 3F(3,3)
Γ <sub>4</sub>	14444.0	14451.0			99		3F(3,±2)
Γ <sub>3</sub>	14456.0				100		3F(3,±2)
Γ <sub>2</sub>	14505.6				100		3F(3,0)
Γ <sub>4</sub>	14981.4	14970.1			76	22	3F(2,±2) 1D(2,±2)

Tm<sup>3+</sup>:YPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	(2S+1)L(J,J <sub>z</sub> ) largest %	(2S+1)L(J,J <sub>z</sub> ) second
Γ <sub>3</sub>	15080.3				77	3F(2,±2)	21 1D(2,±2)
Γ <sub>5</sub>	15093.8	15106.7	1.5		77	3F(2,-1)	21 1D(2,-1)
Γ <sub>1</sub>	15101.4				77	3F(2,0)	21 1D(2,0)
Γ <sub>3</sub>	21035.0	21022.0			57	1G(4,±2)	33 3H(4,±2)
Γ <sub>5</sub>	21170.5		-0.6		39	1G(4,-1)	22 3H(4,-1)
Γ <sub>1</sub>	21216.5				23	1G(4,0)	35 1G(4,±4)
Γ <sub>4</sub>	21286.3	21291.9			57	1G(4,±2)	33 3H(4,±2)
Γ <sub>2</sub>	21296.5				58	1G(4,±4)	33 3H(4,±4)
Γ <sub>5</sub>	21404.0	21404.5	-3.2		39	1G(4,3)	21 3H(4,3)
Γ <sub>1</sub>	21412.1	21433.0			35	1G(4,0)	19 3H(4,0)
Γ <sub>3</sub>	27766.5	27761.0			41	3P(2,±2)	40 1D(2,±2)
Γ <sub>4</sub>	27801.5	27791.3			41	1D(2,±2)	39 3P(2,±2)
Γ <sub>5</sub>	27845.2	27870.0	2.3		41	3P(2,-1)	40 1D(2,-1)
Γ <sub>1</sub>	27869.4				41	1D(2,0)	40 3P(2,0)
Γ <sub>4</sub>	34542.0	34568.0			98	1I(6,±2)	
Γ <sub>5</sub>	34561.3	34556.0	-0.8		60	1I(6,-1)	37 1I(6,3)
Γ <sub>1</sub>	34580.2				71	1I(6,0)	28 1I(6,±4)
Γ <sub>3</sub>	34797.3				90	1I(6,±2)	9 1I(6,±6)
Γ <sub>5</sub>	34806.6	34797.0	-1.8		59	1I(6,3)	28 1I(6,-1)
Γ <sub>2</sub>	34812.0				99	1I(6,±4)	

Tm<sup>3+</sup>:YPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	(2S+1)L(J,J <sub>z</sub> ) % largest	(2S+1)L(J,J <sub>z</sub> ) % second
Γ <sub>1</sub>	34907.6				71	1I(6,±4)	28 1I(6,0)
Γ <sub>4</sub>	34942.3				98	1I(6,±6)	
Γ <sub>3</sub>	34952.1				90	1I(6,±6)	9 1I(6,±2)
Γ <sub>5</sub>	34956.8	34943.0	8.6		85	1I(6,-5)	11 1I(6,-1)
Γ <sub>1</sub>	35236.4	35256.0			93	3P(0,0)	6 1S(0,0)
Γ <sub>2</sub>	36216.3				100	3P(1,0)	
Γ <sub>5</sub>	36299.7	36287.0	3.0		100	3P(1,-1)	
Γ <sub>4</sub>	37877.7				58	3P(2,±2)	38 1D(2,±2)
Γ <sub>5</sub>	38082.1	38069.0	2.6		57	3P(2,-1)	38 1D(2,-1)
Γ <sub>3</sub>	38089.5				56	3P(2,±2)	39 1D(2,±2)
Γ <sub>1</sub>	38094.0				56	3P(2,0)	39 1D(2,0)
Γ <sub>1</sub>	73572.8				94	1S(0,0)	6 3P(0,0)

<sup>a</sup>When the symbol ± appears in front of J<sub>z</sub> the contributions from +J<sub>z</sub> and -J<sub>z</sub> are equal and have been summed. See reference 7 for a description of the eigenvectors of the Γ<sub>i</sub> states.

Table 1b

Observed and calculated energies and g values for  $Tm^{3+}$  in  $LuPO_4$ .

Sym.	Energy ( $cm^{-1}$ )		$g_{\parallel}$		Eig. Composition <sup>a</sup>			
	cal.	obs.	cal.	obs.	( $2S+1$ )L(J, $J_z$ ) %	largest	( $2S+1$ )L(J, $J_z$ ) %	second
$\Gamma_1$	0.0	0.0			71	3H(6,0)	28	3H(6, $\pm 4$ )
$\Gamma_5$	21.9	25.2	4.6	3.3	55	3H(6,-1)	34	3H(6,-5)
$\Gamma_3$	89.9	80.1			97	3H(6, $\pm 2$ )	3	3H(6, $\pm 6$ )
$\Gamma_5$	131.8	124.8	6.7	7.7	62	3H(6,-5)	21	3H(6,-1)
$\Gamma_2$	182.6				99	3H(6, $\pm 4$ )		
$\Gamma_1$	248.2				71	3H(6, $\pm 4$ )	28	3H(6,0)
$\Gamma_4$	254.4				64	3H(6, $\pm 2$ )	35	3H(6, $\pm 6$ )
$\Gamma_5$	281.2		-4.3		73	3H(6,3)	24	3H(6,-1)
$\Gamma_3$	303.0				97	3H(6, $\pm 6$ )	3	3H(6, $\pm 2$ )
$\Gamma_4$	321.4				64	3H(6, $\pm 6$ )	35	3H(6, $\pm 2$ )
$\Gamma_3$	5587.0				62	3F(4, $\pm 2$ )	30	1G(4, $\pm 2$ )
$\Gamma_5$	5682.1	5674.0	-1.5		36	3F(4,-1)	27	3F(4,3)
$\Gamma_1$	5700.2				50	3F(4, $\pm 4$ )	13	3F(4,0)
$\Gamma_2$	5735.3				64	3F(4, $\pm 4$ )	29	1G(4, $\pm 4$ )
$\Gamma_4$	5769.3	5763.0			63	3F(4, $\pm 2$ )	29	1G(4, $\pm 2$ )
$\Gamma_5$	5844.4	5842.0	-3.0		37	3F(4,3)	27	3F(4,-1)
$\Gamma_1$	5856.7				51	3F(4,0)	22	1G(4,0)
$\Gamma_2$	8222.6	8227.0			62	3H(5,0)	38	3H(5, $\pm 4$ )
$\Gamma_5$	8257.7	8262.0	-0.2		67	3H(5,-1)	30	3H(5,3)

Tm<sup>3+</sup>:LuPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>Z</sub> ) %	(2S+1)L(J,J <sub>Z</sub> ) %	largest second
Γ <sub>2</sub>	8384.7	8381.0			38	3H(5,0)	62 3H(5,±4)
Γ <sub>5</sub>	8396.4	8395.0	-0.9		59	3H(5,3)	23 3H(5,-5)
Γ <sub>3</sub>	8425.2				100	3H(5,±2)	
Γ <sub>5</sub>	8444.6	8441.0	7.3		74	3H(5,-5)	16 3H(5,-1)
Γ <sub>1</sub>	12537.0	12530.8			55	3H(4,0)	24 3F(4,0)
Γ <sub>5</sub>	12544.1	12535.2	-3.7	-3.7	45	3H(4,3)	19 3F(4,3)
Γ <sub>5</sub>	12672.6	12657.2	-0.1		44	3H(4,-1)	20 3F(4,-1)
Γ <sub>3</sub>	12676.8				58	3H(4,±2)	28 3F(4,±2)
Γ <sub>2</sub>	12704.7				59	3H(4,±4)	27 3F(4,±4)
Γ <sub>1</sub>	12723.3				54	3H(4,±4)	24 3F(4,±4)
Γ <sub>4</sub>	12782.6	12778.2			59	3H(4,±2)	27 3F(4,±2)
Γ <sub>5</sub>	14404.6	14402.3	-4.3	-5.4	74	3F(3,3)	25 3F(3,-1)
Γ <sub>5</sub>	14429.8	14435.3	0.0		74	3F(3,-1)	25 3F(3,3)
Γ <sub>4</sub>	14438.4	14454.2			99	3F(3,±2)	
Γ <sub>3</sub>	14452.2				99	3F(3,±2)	
Γ <sub>2</sub>	14497.3				100	3F(3,0)	
Γ <sub>4</sub>	14976.7	14964.0			75	3F(2,±2)	22 1D(2,±2)
Γ <sub>5</sub>	15080.5	15087.8	1.5		76	3F(2,-1)	21 1D(2,-1)
Γ <sub>1</sub>	15080.5				77	3F(2,0)	21 1D(2,0)
Γ <sub>3</sub>	15083.8				77	3F(2,±2)	21 1D(2,±2)

Tm<sup>3+</sup>:LuPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>			
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	largest	(2S+1)L(J,J <sub>z</sub> ) %	second
Γ <sub>3</sub>	20991.9	20983.0			57	1G(4,±2)	34	3H(4,±2)
Γ <sub>5</sub>	21133.6		-0.9		37	1G(4,-1)	21	1G(4,3)
Γ <sub>1</sub>	21178.9				21	1G(4,0)	37	1G(4,±4)
Γ <sub>2</sub>	21257.5				57	1G(4,±4)	33	3H(4,±4)
Γ <sub>4</sub>	21267.5	21278.3			57	1G(4,±2)	33	3H(4,±2)
Γ <sub>5</sub>	21381.7	21394.1	-3.0		37	1G(4,3)	21	1G(4,-1)
Γ <sub>1</sub>	21389.5				37	1G(4,0)	20	3H(4,0)
Γ <sub>3</sub>	27755.7	27749.7			41	3P(2,±2)	40	1D(2,±2)
Γ <sub>4</sub>	27793.6	27785.0			41	1D(2,±2)	39	3P(2,±2)
Γ <sub>5</sub>	27818.8	27838.9	2.3		41	3P(2,-1)	41	1D(2,-1)
Γ <sub>1</sub>	27837.6				41	1D(2,0)	40	3P(2,0)
Γ <sub>4</sub>	34576.2	34579.0			97	1I(6,±2)	2	1I(6,±6)
Γ <sub>5</sub>	34595.4	34595.0	-0.9		57	1I(6,-1)	39	1I(6,3)
Γ <sub>1</sub>	34613.4				65	1I(6,0)	33	1I(6,±4)
Γ <sub>2</sub>	34834.3				99	1I(6,±4)		
Γ <sub>3</sub>	34834.6				66	1I(6,±2)	33	1I(6,±6)
Γ <sub>5</sub>	34846.4	34842.0	-0.2		52	1I(6,3)	24	1I(6,-5)
Γ <sub>4</sub>	34911.9				97	1I(6,±6)	2	1I(6,±2)
Γ <sub>3</sub>	34940.2				66	1I(6,±6)	33	1I(6,±2)
Γ <sub>1</sub>	34951.7				33	1I(6,0)	66	1I(6,±4)
Γ <sub>5</sub>	34974.0		7.1		71	1I(6,-5)	20	1I(6,-1)



Tm<sup>3+</sup>:LuPO<sub>4</sub> (continued)

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		Eig. Composition <sup>a</sup>		
	cal.	obs.	cal.	obs.	(2S+1)L(J,J <sub>z</sub> ) %	(2S+1)L(J,J <sub>z</sub> ) %	second
Γ <sub>1</sub>	35224.9	35238.0			93	3P(0,0)	6 1S(0,0)
Γ <sub>2</sub>	36216.9				100	3P(1,0)	
Γ <sub>5</sub>	36276.5	36266.0	3.0		100	3P(1,-1)	
Γ <sub>4</sub>	37862.0				58	3P(2,±2)	38 1D(2,±2)
Γ <sub>5</sub>	38049.4	38045.0	2.6		57	3P(2,-1)	38 1D(2,-1)
Γ <sub>1</sub>	38049.5				58	3P(2,0)	38 1D(2,0)
Γ <sub>3</sub>	38091.4				57	3P(2,±2)	39 1D(2,±2)
Γ <sub>1</sub>	73579.9				94	1S(0,0)	6 3P(0,0)

<sup>a</sup>When the symbol ± appears in front of J<sub>z</sub> the contributions from +J<sub>z</sub> and -J<sub>z</sub> are equal and have been summed. See reference 7 for a description of the eigenvectors of the Γ<sub>i</sub> states.

Table 2

Observed and Calculated energies and g values for Yb<sup>3+</sup> in YPO<sub>4</sub> and LuPO<sub>4</sub>.

Yb<sup>3+</sup>:YPO<sub>4</sub>

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		g <sub>⊥</sub>		Eig. Composition			
	cal.	obs.	cal.	obs.	cal.	obs.	(2S+1)L(2J,2J <sub>z</sub> ) %	largest	(2S+1)L(2J,2J <sub>z</sub> ) %	second
Γ <sub>6</sub>	0.0	0.0	1.7	1.3	3.1	3.2	81	2F(7,-3)	19	2F(7,5)
Γ <sub>7</sub>	90.0	90.0	-0.5		3.8		83	2F(7,-1)	17	2F(7,7)
Γ <sub>6</sub>	305.4		-4.0		3.1		81	2F(7,5)	19	2F(7,-3)
Γ <sub>7</sub>	315.0		-6.4		0.8		83	2F(7,7)	17	2F(7,-1)
Γ <sub>7</sub>	10257.8	10257.8	0.9		2.6		100	2F(5,-1)		
Γ <sub>6</sub>	10258.4	10258.4	0.5		1.8		70	2F(5,-3)	30	2F(5,5)
Γ <sub>6</sub>	10508.5	10508.5	-2.2		1.7		70	2F(5,5)	30	2F(5,-3)

Yb<sup>3+</sup>:LuPO<sub>4</sub>

Sym.	Energy (cm <sup>-1</sup> )		g <sub>  </sub>		g <sub>⊥</sub>		Eig. Composition			
	cal.	obs.	cal.	obs.	cal.	obs.	(2S+1)L(2J,2J <sub>z</sub> ) %	largest	(2S+1)L(2J,2J <sub>z</sub> ) %	second
Γ <sub>6</sub>	0.0	0.0	1.6	1.3	3.2	3.2	80	2F(7,-3)	20	2F(7,5)
Γ <sub>7</sub>	99.0	99.0	-1.1		3.5		76	2F(7,-1)	24	2F(7,7)
Γ <sub>6</sub>	279.3		-3.9		3.2		80	2F(7,5)	20	2F(7,-3)
Γ <sub>7</sub>	288.6		-5.8		1.1		76	2F(7,7)	24	2F(7,-1)
Γ <sub>6</sub>	10244.7	10244.7	0.4		1.8	1.9	68	2F(5,-3)	32	2F(5,5)
Γ <sub>7</sub>	10271.8	10271.8	0.9		2.6	2.5	100	2F(5,-1)		
Γ <sub>6</sub>	10475.5	10475.6	-2.1		1.8		68	2F(5,5)	32	2F(5,-3)

Table 3a

Atomic and crystal field parameters  
for lanthanide ions in YPO<sub>4</sub>.

Param.	Tm <sup>3+</sup>	Yb <sup>3+</sup>
$\zeta$	+2629.9(2)	+2903.0
F <sup>2</sup>	101140.7(33)	
F <sup>4</sup>	70810.2(104)	
F <sup>6</sup>	50095.4(113)	
B <sub>0</sub> <sup>2</sup>	283(22)	339
B <sub>0</sub> <sup>4</sup>	98(51)	72
B <sub>4</sub> <sup>4</sup>	-620(27)	-648
B <sub>0</sub> <sup>6</sup>	-694(40)	-694 <sup>b</sup>
B <sub>4</sub> <sup>6</sup>	4(45)	4 <sup>b</sup>
$\alpha$	15.9(0.3)	
$\beta$	-587(18)	
$\gamma$	2200	
M <sup>0</sup>	4.93 <sup>a</sup>	
M <sup>2</sup>	2.72 <sup>a</sup>	
M <sup>4</sup>	1.37 <sup>a</sup>	
p <sup>2</sup>	729.6 <sup>a</sup>	
p <sup>4</sup>	547.0 <sup>a</sup>	
p <sup>6</sup>	364.0 <sup>a</sup>	
$\sigma$ (cm <sup>-1</sup> )	13.6	

<sup>a</sup>From reference 20.

<sup>b</sup>Fixed at Tm<sup>3+</sup> value.

Table 3b

Atomic and crystal field parameters  
for lanthanide ions in LuPO<sub>4</sub>

Param.	Tm <sup>3+</sup>	Yb <sup>3+</sup>
$\zeta$	+2629.0(1)	+2903.0
F <sup>2</sup>	101250(28)	
F <sup>4</sup>	70754(94)	
F <sup>6</sup>	50051(89)	
B <sub>0</sub> <sup>2</sup>	203(22)	256
B <sub>0</sub> <sup>4</sup>	117(52)	14
B <sub>4</sub> <sup>4</sup>	-673(22)	-608
B <sub>0</sub> <sup>6</sup>	-705(32)	-705 <sup>b</sup>
B <sub>4</sub> <sup>6</sup>	16(33)	16 <sup>b</sup>
$\alpha$	17.5(0.3)	
$\beta$	-635(13)	
$\gamma$	2200	
M <sup>0</sup>	4.93 <sup>a</sup>	
M <sup>2</sup>	2.72 <sup>a</sup>	
M <sup>4</sup>	1.37 <sup>a</sup>	
P <sup>2</sup>	729.6 <sup>a</sup>	
P <sup>4</sup>	547.0 <sup>a</sup>	
P <sup>6</sup>	364.0 <sup>a</sup>	
$\sigma$ (cm <sup>-1</sup> )	10.0	

<sup>a</sup>From reference 20.

<sup>b</sup>Fixed at Tm<sup>3+</sup> value..

Table 4

Zeeman Pattern of the  
 $\Gamma_6$  and  $\Gamma_7$  Excited States for  $\text{Yb}^{3+}:\text{YPO}_4$

---

Predicted Transitions ( $\text{cm}^{-1}$ )	Observed Transitions ( $\text{cm}^{-1}$ )
10262.57	10262.56
10260.09	10260.44
10260.02	10259.67
10258.73	10258.57
10257.33	10257.39
10256.25	10256.46
10256.18	10255.68
10253.99	

---

Table 5  
Crystal Field Parameters for RE:YPO<sub>4</sub> (cm<sup>-1</sup>)

RE	B <sub>0</sub> <sup>2</sup>	B <sub>0</sub> <sup>4</sup>	B <sub>4</sub> <sup>4</sup>	B <sub>0</sub> <sup>6</sup>	B <sub>4</sub> <sup>6</sup>	Ref
*Pr <sup>3+</sup>	78(18)	321(51)	-849(43)	-1376(67)	35(41)	7
*Nd <sup>3+</sup>	302(33)	273(53)	-777(43)	-1245(38)	-109(57)	7
Eu <sup>3+</sup>	362	125	-757	-785	+67	25
Eu <sup>3+</sup>	293	400	-707	-525	-559	22
Ho <sup>3+</sup>	341	-38	-751	-713	-50	25
Er <sup>3+</sup>	279	155	-756	-537	-141	6
*Tm <sup>3+</sup>	283(22)	98(51)	-620(27)	-694(40)	4(45)	**
Yb <sup>3+</sup>	339	72	-648	-694	4	**

\* Values in parentheses are statistical error estimates for the parameters.

\*\* This work.

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