EPR spectroscopic characterization of Gd³⁺ in the monazite-type rare-earth orthophosphates: LaPO₄, CePO₄, PrPO₄, NdPO₄, SmPO₄, and EuPO₄

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The mineral monazite, a mixed lanthanide orthophosphate $Ln PO_4$, is considered as a perfect host for geologic disposal of actinides, rare earths, and possibly other elements formed during nuclear-reactor operation. Synthetic monazite-type orthophosphates of all the elements of the first half of the lanthanide series (except Pm) have been prepared: single crystals were grown using a flux technique, and powders were precipitated in molten urea. The electronparamagnetic-resonance (EPR) spectra of intentionally added Gd impurities show that the Gd³⁺ ions occupy predominantly substitutional rare-earth sites in both the flux-grown single crystals and the precipitated powders. Though these sites have a very low (triclinic C_1) symmetry, the spectra were successfully interpreted using an orthorhombic spin Hamiltonian. It has been found that, while the main spin-Hamiltonian parameter b_2^0 is almost constant when going from the LaPO₄ to the EuPO₄ host $(b_2^0 \approx +830 \times 10^{-4} \text{ cm}^{-1})$, the parameter b_2^2 decreases monotonically from $+373 \times 10^{-4}$ to $+283 \times 10^{-4}$ cm⁻¹, respectively. The complete analysis (i.e., angular variations of the EPR lines and position of the principal electric field axes relative to the crystallographic axes) of the EPR single-crystal spectra has been done for the two diamagnetic hosts $LaPO_4$ and $EuPO_4$, where the observed EPR lines are the sharpest. It is shown, in particular, that the two magnetically inequivalent EPR spectra (i.e., 14 lines) observed for the monazitetype single crystals are in fact equivalent when the magnetic field is applied parallel or perpendicular to the b axis of the monoclinic structure (i.e., for these directions, only seven degenerate lines are observed). These results are in perfect agreement with the description of the monazite structure whose unit cell contains four "different" rare-earth sites that transform with the symmetry operations of the C_{2h} group. The present investigation constitutes an indispensable basis for subsequent studies of actinide-doped monazite orthophosphates or of α -induced radiation damage in these hosts.

I. INTRODUCTION

Materials for the primary containment of long-lived radioactive wastes must satisfy a number of stringent criteria. These criteria include high retention of actinide and other radioactive ions at the elevated temperatures associated with useful concentrations of nuclear waste, long-term chemical and physical stability under the conditions that can exist in a geological repository, and resistance to α -particle and recoil radiation damage. The various possible scenarios adherent to storage in a deep geological formation include exposure of the waste form to hydrothermal conditions. Recent findings^{1, 2} have indicated that borosilicate glasses which have been seriously considered as primary radioactive waste forms are, in fact, both chemically and physically unstable under hydrothermal conditions, and these results have prompted a reconsideration of alternative crystalline materials for the containment of nuclear wastes. One class of crystalline materials that appears to be particularly attractive, especially for the isolation of α active actinide wastes, is represented by the monoclinic lanthanide orthophosphates. These materials are analogs of the mixed orthophosphate mineral monazite, a natural crystalline substance with an established long-term ($\sim 10^9$ yr) stability in nature,³ a known capacity for the incorporation of relatively high concentrations of the actinides Th and U,^{4, 5} and a relatively high resistance to metamictization.^{6, 7}

Due to the special combination of characteristics noted above, the chemical and physical properties of the lanthanide orthophosphates are currently the subject of extensive investigations.⁸ These investigations include examinations of iron-group, rare-earth, and actinide impurities in order to obtain information regarding their valence states, crystalline site symmetries, and other solid-state properties. The goal of these studies is to relate the fundamental properties of mixed orthophosphate-impurity systems to the features that determine their suitability as a primary waste form.

The lanthanide orthophosphates formed from elements in the first half of the transition series (i.e., La through Gd) are characterized by the monoclinic, monazite structure (space group $P2_1/n$), while those

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formed by elements in the second half of the series (i.e., Tb through Lu plus Y and Sc) have the tetragonal structure typical of the mineral zircon.9,10 The results of EPR investigations of Gd³⁺ in the tetragonal-symmetry orthophosphates LuPO₄, YPO₄, and ScPO₄ have been reported elsewhere.¹¹ The purpose of the present work is to present the results of EPR investigations of Gd³⁺ in single crystals and powders of the monoclinic lanthanide orthophosphates. These results are compared with the structural data obtained from single-crystal x-ray-diffraction investigations and provide information concerning the local symmetry at the Gd site. Additionally, comparisons of the single crystal and powder spectra of Gd³⁺ provide a technique for monitoring complex chemical and physical processing sequences. This technique can be used to show that an impurity like Gd³⁺ has not become associated with local point defects or converted to an interstitial site during processing.

In Sec. II the techniques for preparation of both powder and single-crystal samples of the orthophosphates will be outlined and the crystal structure and habit will be discussed. A description of the theory appropriate to the case of Gd^{3+} in an orthorhombic site is given in Sec. III. The experimental results are presented in Sec. IV, and their implications are treated in Sec. V.

II. EXPERIMENTAL

A. Sample preparation

The monoclinic lanthanide orthophosphate single crystals and powders employed in the present series of investigations were prepared using techniques similar to those described in Ref. 11 for the preparation of the tetragonal zircon-structure orthophosphates. Accordingly, this aspect of the experimental procedure is only briefly described in the following discussion.

Single crystals of $Ln PO_4$ with Ln = La, Ce, Pr, Nd, Sm, and Eu were grown by means of a flux technique similar to that initially described by Feigelson.¹² A standard starting composition consisting of 3.5 g of the corresponding lanthanide oxide, 0.1 mol% Gd_2O_3 , and 60 g of PbHPO₄ was used. This mixture was placed in a 50-cm³ platinum crucible with a tight-fitting Pt lid and heated to 1360 °C. The temperature was maintained at this value for 16 h and then slowly reduced to 900 °C at a rate of 1 °C/h. The resulting crystals were removed by a slow dissolution of the solidified flux by boiling in nitric acid.

Powders of the lanthanide orthophosphates were precipitated by means of the urea process described in detail in Ref. 13. In this procedure, the corresponding lanthanide oxide powder Ln_2O_3 was mixed with 1 mol% Gd₂O₃ and then dissolved in a dilute nitric acid solution. (It should be noted that for the case of cerium, cerium nitrate was used in place of the oxide, since the stable oxide CeO_2 does not readily dissolve in HNO_3 .) The addition of a stoichiometric amount of ammonium hydrogen phosphate $[(NH_4)_2HPO_4]$ to the solution results in the formation of the lanthanide orthophosphate LnPO₄ by a metathesis reaction. A variation in the amount of urea $[(NH_2)_2CO]$ added during the precipation phase of the process can be used to control the final phosphate particle size in the powder. Calcination of the precipitate at 800 °C removes the excess urea, and very fine powders (particle size $\leq 0.1 \ \mu m$) can be obtained. Compaction of these powders with an appropriate particle size by hot pressing at 1000 °C and 4000 psi resulted in pellets whose density was about 97% of the theoretical value.¹³ X-ray analysis was used to verify that the phosphate powders produced by means of this technique had the same monoclinic monazite structure as the flux-grown single crystals.

B. Crystal structure and crystal habit

X-ray studies of natural monazite and monazitetype crystals have been carried out by a number of authors.^{7, 14–16} Although the values for the lattice parameters determined in these investigations were generally in good agreement, Wyckoff¹⁰ has pointed out a number of discrepancies concerning the actual positions of the atoms in the unit cell. Ueda¹⁵ has reexamined this structure, and he concluded that these apparent discrepancies were simply due to a translation of the lattice origin by $\frac{1}{2}b$. Additional confusion can arise in this case due to the fact that in the monoclinic structure, the axis perpendicular to the two nonorthogonal axes is called the b axis, but in a hexagonal structure it is labeled as the c axis. This strange crystallographic convention can sometimes result in a left-handed coordinate system, and this appears to be the case in Fig. 3 of the article by Mooney-Slater.¹⁴ Projections of the monazite structure on the (010) and (001) planes made according to the results of recent x-ray studies of pure CePO₄ single crystals¹⁷ are shown in Fig. 1. In this structure, the unit cell is monoclinic, with space group $P2_1/n$, and contains four molecules. Each Ce ion is surrounded by nine oxygen nearest neighbors. The four different cerium sites with their associated oxygen nearest neighbors are shown in Fig. 2, together with the list of symmetry operations that transform one site into another. As can be seen in Fig. 2, the local point symmetry at a particular cerium site is reduced to the identity (C_1) . The distances $Ce^{3+}-O^{2-}$, as determined in Ref. 17, vary from 2.445 to 2.779 Å, and even the phosphate tetrahedra are somewhat distorted. Considering the complicated, lowsymmetry nature of this structure, it is clear that EPR investigations of these materials will involve the



FIG. 1. Projections of the monazite crystal structure on the *ac* plane [(010) plane] and the *ab* plane [(001) plane]. Positions of the atoms have been reported according to recent refinements of the crystal structure carried out by Beall et al. (Ref. 17) using pure $CePO_4$ single crystals. The PO_4 tetrahedra and the Ln ions are arbitrarily labeled 1 to 4. It should be noted that in the monoclinic structure the axis perpendicular to the other two nonorthogonal axes is called the b axis (i.e., it is not termed the c axis).

determination of a relatively large number of spin-Hamiltonian parameters and, in general, will be considerably more difficult than analogous investigations of the tetragonal-symmetry orthophosphates¹¹ occurring in the second half of the rare-earth series. Additionally, as described in Sec. IV B, the unit cell of the monazite structure contains two magnetically inequivalent sites. A further complication arises from the fact that, for Gd³⁺ in the monazite-structure materials, the crystalline-electric-field axes do not coincide with the crystallographic axes.

EPR investigations of the monazite-structure lanthanide orthophosphates are also complicated by the observation that the external faces of crystals produced by means of the flux technique described previously are not simply related to the crystallographic axes. Laue back-reflection x-ray photographs were required in order to identify the b axis (i.e., the twofold symmetry axis) of the monoclinic crystal. Following this identification, the crystal was mounted in the EPR cavity (see Sec. IV B) with the b axis per-



Ln2 Ln3

REFLECTION ABOUT THE (010) PLANE Ln4

INVERSION

FIG. 2. Positions of the nine oxygen nearest neighbors surrounding the four different rare-earth sites contained in the unit cell of the monazite structure. This figure has been drawn by considering the packing diagram shown in Fig. 1. From a crystallographic point of view, all four sites are equivalent since the symmetry operations listed above can transform any one given site into another. From the EPR point of view, however, as is shown in Sec. IV B, sites (1) and (4) are magnetically equivalent, as are sites (2) and (3). The symmetry operation which changes the single-crystal EPR spectrum of sites (1,4) into the spectrum of sites (2,3) is a 180° rotation about the *b* axis.

pendicular to the plane in which the applied magnetic field was rotated, and this configuration was used in measuring the angular variation of the EPR spectrum in the (010) plane. The sample was also mounted with the b axis in the plane of the applied magnetic field, in order to determine the principal axes of the crystalline electric field. Subsequent x-ray measurements using a precession camera were employed to distinguish the *a* axis from the *c* axis and ultimately to determine the angles between these two crystallographic directions and the crystal-field principal axes.

Typical crystal habits of the monazite-type rare-



FIG. 3. Schematic representation of the crystal habit of monazite-type rare-earth orthophosphates as grown using the flux technique described in Sec. II A. The first three orthophosphates of the lanthanide series, LaPO₄, CePO₄, and PrPO₄, have the crystal habit shown here for the LaPO₄ case. The faces labeled C and D are almost perpendicular, but neither face corresponds to a (010) plane (i.e., the plane perpendicular to the b axis). The b axis lies in the face labeled B (shaded in the figure) and is perpendicular to the long edge of that face. This face is not developed in all crystals, but the b axis can still be identified from faces A and C, which make an angle of 75°. The three monazite-type orthophosphates NdPO₄, SmPO₄, and EuPO₄ are characterized by the plateletlike shape shown here for the EuPO₄ case, with the b axis lying in the face of the platelet and perpendicular to one edge.

earth orthophosphates, which are shown in Fig. 3, along with the direction of the b axis, can be roughly described as follows:

(i) The three orthophosphate crystals LaPO₄, CePO₄, and PrPO₄ have a complicated polyhedral shape which usually exhibits one set of perpendicular faces. These perpendicular faces do not correspond to $\{100\}$ planes, however; i.e., the *b* axis is not perpendicular to one of these faces but is contained in a small face (shaded in Fig. 3) and is perpendicular to the long edge of that face. It should be noted that, with the flux growth technique described in Sec. II A, the shaded face containing the *b* axis is not present in all crystals.

(ii) The three orthophosphate crystals $NdPO_4$, SmPO₄, and EuPO₄ are characterized by a plateletlike shape, with the *b* axis lying in the face of the platelet, perpendicular to one of the edges.

III. THEORY

Trivalent gadolinium is characterized by a $4f^7$ electronic configuration and an associated ${}^8S_{7/2}$ Hund's rule ground state. The EPR spectrum of an ${}^8S_{7/2}$ ion in a crystalline electric field can be described by

means of the following general spin Hamiltonian:

$$\mathcal{K} = g \,\mu_B \vec{\mathbf{H}} \cdot \vec{\mathbf{S}} + \sum_{n,m} b_n^m O_n^m \quad , \tag{1}$$

where μ_B is the Bohr magneton, the O_n^m are Stevens's operator equivalents, and the b_n^m are corresponding spin-Hamiltonian parameters. The summation over *m* and *n* can be greatly reduced by considering the local symmetry of the neighbors surrounding the paramagnetic impurity. In the case of orthorhombic symmetry (i.e., with three orthogonal C_2 symmetry axes), the spin Hamiltonian of Eq. (1) takes the following form:

$$\mathfrak{K} = g \,\mu_B \vec{\mathbf{H}} \cdot \vec{\mathbf{S}} + \frac{1}{3} \left(b_2^0 O_2^0 + b_2^2 O_2^2 \right) \\ + \frac{1}{60} \left(b_4^0 O_4^0 + b_4^2 O_4^2 + b_4^4 O_4^4 \right) \\ + \frac{1}{1260} \left(b_6^0 O_6^0 + b_6^2 O_6^2 + b_6^4 O_6^4 + b_6^6 O_6^6 \right) \quad . (2)$$

Additionally, with this type of symmetry, the principal electric field x, y, and z axes must be the three orthogonal C_2 axes of the local point group symmetry.

As noted in Sec. II B, the local symmetry at a Ce site in the monazite structure is lower than orthorhombic (triclinic C_1 symmetry), and, consequently, the principal electric field axes can no longer be deduced by direct inspection of the local structure. There are two possible alternatives in this case: the choice of the x, y, and z axes of the coordinate system is arbitrary and, in that case, the summation in Eq. (1) must include imaginary terms as well as odd m terms; or, the axes are chosen so that they correspond to the "principal" crystalline electric field axes. The second alternative was chosen in the present case, and an experimental determination of the "principal axes" was performed according to the following rules. The direction of the applied magnetic field \overline{H} that corresponds to the absolute extreme of the EPR line positions was chosen as the z axis. The direction corresponding to a relative extreme was then chosen as either the x or the y axis, depending on the convention used. In a coordinate system chosen in this manner, the orthorhombic spin Hamiltonian [Eq. (2)] can still be applied to an ${}^{8}S_{7/2}$ ion in a site whose symmetry is lower than orthorhombic since the additional terms are generally small. The applicability is confirmed in the present case of Gd³⁺ in LnPO₄ by the agreement between the single crystal and powder EPR spectra, and the spectral features predicted using Eq. (2) and the parameters listed In Tables I and II.

When the applied magnetic field \overline{H} is oriented along the principal electric field z axis, the magnetic field positions of the seven allowed transitions $M_s \rightarrow M_s - 1$ are given by the following second-order expressions¹⁸:

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$$(\pm \frac{7}{2}) \leftrightarrow (\pm \frac{5}{2}) H_{\pm 7/2,z} = (g\mu_B)^{-1} (h\nu \mp (6b_2^0 + 20b_4^0 + 6b_6^0) + E' \{ [45/(1 \pm 3F)] - [21/(1 \pm 5F)] \}) ,$$

$$(\pm \frac{5}{2}) \leftrightarrow (\pm \frac{3}{2}) H_{\pm 5/2,z} = (g\mu_B)^{-1} (h\nu \mp (4b_2^0 - 10b_4^0 - 14b_6^0) + E' \{ [60/(1 \pm F)] - [21/(1 \pm 5F)] - [45/(1 \pm 3F)] \}) ,$$

$$(\pm \frac{3}{2}) \leftrightarrow (\pm \frac{1}{2}) H_{\pm 3/2,z} = (g\mu_B)^{-1} (h\nu \mp (2b_2^0 - 12b_4^0 + 14b_6^0) + E' \{ [21/(1 \pm 5F)] - [45/(1 \pm 3F)] \}) ,$$

$$(\pm \frac{1}{2}) \leftrightarrow (-\frac{1}{2}) H_{\pm 3/2,z} = (g\mu_B)^{-1} (h\nu \mp (2b_2^0 - 12b_4^0 + 14b_6^0) + E' \{ [21/(1 \pm 5F)] - [45/(1 \pm 3F)] \}) ,$$

$$(\pm \frac{1}{2}) \leftrightarrow (-\frac{1}{2}) H_{1/2,z} = (g\mu_B)^{-1} (h\nu + E' \{ [90/(1 - 9F^2)] - [120/(1 - F^2)] \}) ,$$

where

$$E' = (b_2^2)^2 / (18g \mu_B H)$$
 and $F = b_2^0 / g \mu_B H$

From Eq. (3), the g value can be simply deduced from the expression

$$g = \frac{4h\nu}{\mu_B} \left(H_{7/2,z} + H_{-7/2,z} + H_{3/2,z} + H_{-3/2,z} \right)^{-1} , \quad (4)$$

since second-order terms in b_2^2 vanish in Eq. (4) above. The diagonal spin-Hamiltonian parameters b_n^0 can be easily determined by measuring the three magnetic field separations between sets of two appropriately selected transitions as indicated below:

$$\Delta H_{7/2,z} = |H_{7/2,z} - H_{-7/2,z}|$$

$$= (1/g \,\mu_B) (12b_2^0 + 40b_4^0 + 12b_6^0) ,$$

$$\Delta H_{5/2,z} = |H_{5/2,z} - H_{-5/2,z}|$$

$$= (1/g \,\mu_B) (8b_2^0 - 20b_4^0 - 28b_6^0) ,$$

$$\Delta H_{3/2,z} = |H_{3/2,z} - H_{-3/2,z}|$$

$$= (1/g \,\mu_B) (4b_2^0 - 24b_6^0 + 28b_6^0) .$$
(5)

[Terms of the order of E'F have been omitted in Eqs.

(4) and (5).] In the plane perpendicular to the z axis, the magnetic field separations between these pairs of transitions are given to first order by

. .

$$\Delta H_{7/2,1} = (6b_2^0 - 15b_4^0 + \frac{15}{4}b_6^0 - 6b_2^2 \cos 2\phi - 5b_4^4 \cos 4\phi)(g\mu_B)^{-1} ,$$

$$\Delta H_{5/2,1} = (4b_2^0 + \frac{15}{2}b_4^0 - \frac{35}{4}b_6^0 - 4b_2^2 \cos 2\phi + \frac{5}{2}b_4^4 \cos 4\phi)(g\mu_B)^{-1} ,$$

$$\Delta H_{3/2,1} = (2b_2^0 + 9b_4^0 + \frac{35}{4}b_6^0 - 2b_2^2 \cos 2\phi + 3b_4^4 \cos 4\phi)(g\mu_B)^{-1} ,$$

(6)

where ϕ is the angle between the magnetic field and the x axis. It should be noted that the choice of the x and y axes depends on the choice of the sign of b_2^2 , and, usually, the convention is that the greatest extreme of the position the EPR lines in the plane $\overline{H}_{\perp z}$ corresponds to the y axis. The off-diagonal parameters b_2^2 and b_4^4 can be determined using Eq. (6). The remaining off-diagonal parameters $(b_4^2, b_6^2, b_6^4, and$ $<math>b_6^6)$, which have been omitted in Eq. (6), are more difficult to obtain and are usually neglected since they

TABLE I. Spin-Hamiltonian parameters for $Ln \operatorname{PO}_4$:Gd³⁺ powders and x-ray-crystallographic data. Crystallographic data are taken from Refs. 16, 17, and 22. Numbers in parentheses represent the estimated errors in the last place. The b_n^m are in the units of 10^{-4} cm⁻¹, ϵ is defined in Eq. (8), and *a*,*b*,*c* are in Å.

	LaPO ₄	CePO ₄	PrPO ₄	NdPO ₄	SmPO ₄	EuPO ₄
	1.995(2)	1.995(2)	1.995(2)	1.991(2)	1.991(2)	1.992(2)
b_{2}^{0}	+834(5)	+828(5)	+837(5)	+840(5)	+830(5)	+834(5)
b_{4}^{0}	-1.4(3)	-1.6(3)	-1.2(3)	-1.4(3)	0.0(3)	0.0(3)
b_{6}^{0}	-0.1(2)	-0.2(2)	+0.2(2)	-0.1(2)	-0.6(2)	+0.3(2)
b_2^2	+373(5)	+336(5)	+323(5)	+306(5)	+288(5)	+283(5)
b_{4}^{4}	-18(4)	-22(4)	-27(4)	-40(4)	-50(4)	-51(4)
E	0.0058	0.0074	0.0097	0.0256	0.016	0.0135
а	6.89	6.777	6.75	6.73	6.67	6.61
b	7.05	6.993	6.94	6.91	6.86	6.81
с	6.48	6.445	6.40	6.38	6.32	6.29
β	103.5°	103.5°	103.5°	103.5°	103.5°	103.5°

TABLE II. Spin-Hamiltonian parameters deter	mined us-
ing EuPO ₄ :Gd ³⁺ and LaPO ₄ :Gd ³⁺ single crystals.	All b_n^m are
given in units of 10^{-4} cm ⁻¹ . Numbers in parenth	neses
represent the estimated errors in the last place.	

	LaPO ₄	EuPO ₄
g	1.994(1)	1.991(1)
69	+831(5)	+829(5)
$b_{\mathbf{A}}^{\tilde{0}}$	-0.9(3)	+0.2(3)
Ьġ	-0.2(2)	-0.2(2)
b 3	+370(5)	+287(5)
b 4	-24(4)	-49(4)
e	0.0065	0.0038

are generally so small that they are not well determined within the experimental errors.

The previous considerations for a single paramagnetic impurity in a given symmetry site are, of course, valid for sites which are identical within a translation operation (i.e., for a given site in a single crystal). The corresponding EPR "powder spectrum" (i.e., the spectrum observed for a polycrystalline specimen) must represent an average, over all possi-

ble magnetic field orientations, of the various singlecrystal lines. Considering the complex form of the orthorhombic spin Hamiltonian of Eq. (2), an exact calculation of this average is difficult, and it has been shown¹⁸ that the main features of the EPR "powder" spectrum can be described very well by simply considering only the principal terms $b_2^0 O_2^0$ and $b_2^2 O_2^2$. When these two terms are averaged over all possible magnetic field orientations, each allowed transition $\pm M_s \leftrightarrow \pm M_s \mp 1 \ (M_s = \frac{7}{2}, \frac{5}{2}, \frac{3}{2})$ is averaged between two shoulders, whose magnetic field positions are the same as those of the corresponding single-crystal line when \vec{H} is applied along the z and y axes. Between these two shoulders, a divergence also appears that is positioned at the magnetic field value of the corresponding single-crystal EPR line when \vec{H} is parallel to the x axis. A satisfactory description of the properties of the "central" $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ EPR transition is more difficult, since the average over all possible magnetic field orientations must be carried out to second order and depends on the ratio b_2^2/b_2^0 . If this ratio is larger than $\frac{1}{3}$ (corresponding to $\lambda = b_2^2/3b_2^0$ $>\frac{1}{9}$ in Ref. 18), as is the case for all of the Ln PO₄:Gd³⁺ systems investigated here, then the principal features of this central transition in the powder spectrum are

one shoulder positioned at $(h\nu/g\mu_B)\left[1 + \frac{20}{3}\left(1 + b_2^2/b_2^0\right)(b_2^0/h\nu)^2\right]$, one divergence positioned at $(h\nu/g\mu_B)\left[1 + \frac{20}{3}\left(1 - b_2^2/b_2^0\right)(b_2^0/h\nu)^2\right]$, one divergence positioned at $(h\nu/g\mu_B)\left\{1 - \frac{10}{3}\left[1 - (b_2^2/b_2^0)^2\right](b_2^0/h\nu)^2\right\}$, one shoulder positioned at $(h\nu/g\mu_B)\left[1 - \frac{15}{4}\left(1 + b_2^2/3b_2^0\right)^2(b_2^0/h\nu)^2\right]$.

(7)

It should be noted that two other small shoulders are also present in the "powder" spectrum of the central transition. One of these is approximately positioned at $H_0 = h\nu/g\mu_B$ [the exact position is $(h\nu/g\mu_B)[1 - \frac{15}{9}(b_2^2/h\nu)^2]$] and corresponds to the single-crystal central line when \vec{H} is parallel to the z axis.

IV. RESULTS

A. $Ln PO_4: Gd^{3+}$ powders

The technique of precipitation in molten urea discussed in Sec. II A was used to prepare monazite-type orthophosphate powders of all of the elements in the first half of the lanthanide series (except Pm and Gd itself). An addition of 1 mol% Gd_2O_3 prior to the dissolution in nitric acid directly provided doped powders following the calcination at 800 °C. X-raydiffraction measurements were performed in order to verify the structure of the precipitated orthophosphate powders, and only the monoclinic monazite phase was present after the calcination. This result is in agreement with the observations of Bondar' *et al.*,⁹ who showed that precipitated orthophosphate powders of the first half of the lanthanide series are characterized by a hexagonal low-temperature form which is irreversibly transformed into the stable higher-temperature monoclinic phase at temperatures ranging from 400 to 550 °C. Therefore, a hightemperature process such as calcination at 800 °C or a flux growth of single crystals produces only the monoclinic monazite phase.

The EPR spectra observed at K_a band (~35 GHz) and room temperature for Gd³⁺ in the $Ln PO_4$ precipitated powders are shown in Figs. 4 to 9. Prior to these measurements, the powders were heated with a torch to remove any adsorbed water, in order to improve the Q factor of the EPR microwave cavity. The amount of adsorbed water can be considerable, due to the small particle size ($\leq 0.1 \mu m$) of these urea-precipitated powders. As can be seen in Figs. 4–9, the EPR powder spectra for the various ortho-



FIG. 4. EPR spectrum of LaPO₄:Gd³⁺ powder prepared using the technique of precipitation in molten urea (see Sec. II A). The seven allowed transitions $M_s \leftrightarrow (M_s - 1)$ are labeled with the letters a-g. The subscript x is used to identify the divergences whose magnetic field positions are identical to those of the corresponding single-crystal lines when \vec{H} is parallel to the principal electric field x axis. The y and z subscripts label the shoulders corresponding, respectively, to the relative and absolute extremes of the positions of the EPR single-crystal lines (i.e., the transitions observed with $\vec{H} \parallel y$ and $\vec{H} \parallel z$, respectively).



FIG. 5. EPR spectrum of a urea-precipitated powder of CePO₄:Gd³⁺. The x divergences are labeled with arrows, while the y and z shoulders are identified by bars at the bottom of the figure. The heights of both the shoulder bars and divergence arrows are drawn in proportion to the theoretical intensity of the corresponding EPR single-crystal transitions: i.e., 7:12:15:16:15:12:7 for the $M_s \leftrightarrow (M_s - 1)$ transitions with $M_s = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$, respectively. Due to the magnetic ground state of Ce³⁺, the EPR lines of Gd³⁺ are broadened considerably as compared with the lines observed for Gd³⁺ in the LaPO₄ powder (see Fig. 4).



FIG. 6. EPR spectrum of a urea-precipitated powder of $PrPO_4:Gd^{3+}$. The position of the y and z shoulders, which are identified with bars at the bottom of the figure, are used in calculating the spin-Hamiltonian parameters listed in Table I. Then, using these parameters, the positions of the x divergences, as well as the positions of the different features of the central transition $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ [cf. Eqs. (7)], were predicted and are indicated by arrows at the bottom of the figure.

phosphate hosts cover a span of more than $10\,000$ G and are characterized by shoulders and divergences whose positions are very similar in going from one host to another. Due to the magnetic properties of the rare earths, however, the linewidths of these features are quite different. The LaPO₄:Gd³⁺ and

 $EuPO_4:Gd^{3+}$ spectra are characterized by sharp lines, since the ground states for both La^{3+} and Eu^{3+} are nonmagnetic. In contrast to this situation, the linewidths for the other systems, where the rare earths possess magnetic ground states, are considerably broader.



FIG. 7. EPR spectrum of a urea-precipitated powder of NdPO₄:Gd³⁺. The shoulders and the divergences are characterized by magnetic field positions which are very close to those found for Gd^{3+} in LaPO₄ (see Fig. 4), but the linewidths of these features are considerably broadened due to the magnetic ground state of Nd³⁺.



FIG. 8. EPR spectrum of a SmPO₄:Gd³⁺ powder prepared using the technique of precipitation in molten urea as described in Sec. II A. The features of the central transition $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ are more intense and were recorded using a reduced gain.



FIG. 9. EPR spectrum of a EuPO₄Gd³⁺ urea-precipitated powder. Due to the fact that Eu³⁺ is characterized by a 4/⁶ unfilled shell, its ⁷F₀ ground state is nonmagnetic, and therefore the linewidths of Gd³⁺ in EuPO₄ are comparable to those in the LaPO₄:Gd³⁺ powder sample (see Fig. 4). The positions of the z shoulders do not vary appreciably in going from LaPO₄:Gd³⁺ to EuPO₄:Gd³⁺, since b_2^0 is almost constant for all of these monazite-type orthophosphates (see Table I). The positions of the y shoulders and x divergences do vary slightly with the b_2^2 spin-Hamiltonian parameter. The extra shoulder, which appears in the central transition $+\frac{1}{2} \rightarrow -\frac{1}{2}$ near the arrow labeling the g value, corresponds to the single-crystal central line when \vec{H} is parallel to the principal electric field z axis.

The y and z shoulders for the different transitions are identified by bars at the bottom of Figs. 4-9. The heights of these bars have been drawn in proportion to the theoretical intensities of the corresponding single-crystal transitions. For each spectrum, the magnetic field position of these shoulders was determined by calibrating the magnetic field sweep with a least-squares fit to seven different proton NMR frequencies between 7 000 and 14 000 G. The six relations listed in Eqs. (5) and (6) were then used to calculate the five spin-Hamiltonian parameters b_2^0 , b_2^2 , b_4^0 , b_4^4 , and b_6^0 by means of a least-squares fit to the six experimental splittings $\Delta H_{M,y}$ and $\Delta H_{M,z}$ with $M = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$. The resulting parameters are listed in Table I, together with deviations between the experimentally determined magnetic field splittings and the values predicted using the calculated parameters. The deviation ϵ is defined by the following expression

$$\boldsymbol{\epsilon} = \left[\sum_{M,i} \left(\frac{\Delta H_{M,i}^{\text{expt}} - \Delta H_{M,i}^{\text{calc}}}{\Delta H_{M,i}^{\text{expt}}} \right)^2 \right]^{1/2} , \qquad (8)$$

where $M = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$ and i = y, z.

The g values listed in Table I were determined from Eq. (4). According to intensity measurements performed at K band (24 GHz) and 1.5 K, using LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ single crystals, the sign of b_2^0 was determined to be positive and has been assumed to be positive for all of the remaining monoclinic orthophosphate hosts. EPR measurements on the isostructural systems $Ln_2(SO_4)_3 \cdot 8H_2O:Gd^{3+}$ with Ln = Pr, Nd, Sm, Eu indicated¹⁹ that the sign of b_2^0 was positive for the samarium salt and negative for the other compounds. An attempt was made to measure the sign of b_2^0 for the SmPO₄:Gd³⁺ system, but it is believed that a magnetic-phase transition occurs between room and helium temperature, which prevented an observation of the Gd fine-structure lines at low temperature. The sign of b_2^2 was chosen in accordance with the convention mentioned in Sec. III.

Following the calculation of spin-Hamiltonian parameters from the observed positions of the y and z shoulders, positions of the x divergences were predicted, and these positions are indicated by arrows in Figs. 4-9. The two shoulders and the two divergences labeled "d" on these figures are features predicted for the central transition $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ [of Eq. (7)]. The extra shoulder, which is observed near the arrow indicating the g value, is located at the magnetic field position of the single-crystal central transition when \vec{H} is parallel to z.

As can be seen in Figs. 4–9, all of the features present in the EPR powder spectra of Gd^{3+} -doped monazite-type $Ln PO_4$ can be explained using the orthorhombic spin Hamiltonian of Eq. (2) and one set of spin-Hamiltonian parameters. Therefore, it is possible to conclude that, in these lanthanide orthophosphates, Gd^{3+} ions predominantly occupy one crystallographic site, which is most likely to be the Ln^{3+} substitutional site. This assumption is verified in the following section, where a complete analysis of the single-crystal EPR spectra is carried out for the LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ systems.

B. LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ single crystals

A complete analysis of the single-crystal EPR spectra, i.e., a determination of the spin-Hamiltonian parameters and principal crystalline-electric-field axes, was not carried out for all of the $Ln PO_4:Gd^{3+}$ systems. As is evident in the powder spectra shown in Figs. 4–9, the linewidths of the various EPR transitions are too broad to permit an accurate determination of the crystalline-electric-field axes for the Ce, Pr, Nd, and Sm orthophosphates. Consequently, only the first and the last monoclinic orthophosphates of the lanthanide series (i.e., LaPO₄ and EuPO₄) were completely analyzed. These hosts are characterized by the narrowest Gd³⁺ EPR linewidths.

We shall assume, as previously stated, that all the Gd^{3+} -doped ions occupy Ln^{3+} substitutional sites. Since the unit cell of the monazite structure contains four different $Ln PO_4$ molecules (see Figs. 1 and 2), when Gd^{3+} ions occupy substitutional Ln sites, the single crystal will be characterized by four "different" Gd³⁺ sites, which must be equally probable. As can be seen in Fig. 2, the symmetry operations which transform one site into another are: (1) the identity, (2) a 180° rotation along the b axis of the crystal, (3) a reflection on the plane perpendicular to the b axis, and (4) inversion. It is clear that the four sets of principal electric field axes associated with these four sites must also transform via the same symmetry operations. In the following discussion, an orthogonal (c^*ab) reference system will be employed for the crystal $(c^* = a \times b)$, so that the third axis of this orthogonal system is identical to the b axis of the crystal structure. If the principal electric field axes attached to the site (1) in this reference system are characterized by the direction cosines $(\alpha_i^1, \beta_i^1, \gamma_i^1)$, where the *i* index denotes the three electric field x, y, and z axes, then the three remaining sets of electric field axes attached to the other sites have the following direction cosines:

$$(\alpha_i^2, \beta_i^2, \gamma_i^2) = (-\alpha_i^1, -\beta_i^1, \gamma_i^1) \text{ for site } (2) (180^\circ \text{ rotation}) ,$$
$$(\alpha_i^3, \beta_i^3, \gamma_i^3)$$

=
$$(\alpha_i^1, \beta_i^1, -\gamma_i^1)$$
 for site (3) (reflection) , (9)

$$(\alpha_i^4, \beta_i^4, \gamma_i^4)$$

= $(-\alpha_i^1, -\beta_i^1, -\gamma_i^1)$ for site (4) (inversion).

When a magnetic field \vec{H} , whose direction cosines are (k,l,m) in the (c^*ab) reference system, is applied, then the angles between \vec{H} and the electric field axes are given by

$$\theta_i^{1} = \arccos(\alpha_i^{1}k + \beta_i^{1}l + \gamma_i^{1}m) ,$$

$$\theta_i^{2} = \arccos(-\alpha_i^{1}k - \beta_i^{1}l + \gamma_i^{1}m) ,$$

$$\theta_i^{3} = \arccos(\alpha_i^{1}k + \beta_i^{1}l - \gamma_i^{1}m) = \pi + \theta_i^{2} ,$$

$$\theta_i^{4} = \arccos(-\alpha_i^{1}k - \beta_i^{1}l - \gamma_i^{1}m) = \pi + \theta_i^{1} .$$

(10)

Using Eq. (10) it can be shown that sites (1) and (4) are magnetically equivalent, as are sites (2) and (3), and that for a general orientation of the magnetic field, two EPR spectra (i.e., 14 lines) should be observed for Gd^{3+} -doped monazite-type orthophosphate single crystals. The two sets of magnetically equivalent Gd^{3+} sites (1,4) and (2,3), will therefore be labeled only with the index (1) and (2), respectively.

The four Gd³⁺ sites will all be magnetically equivalent for the following special orientations of the applied magnetic field \vec{H} : (i) when \vec{H} is applied along the *b* axis of the crystal; i.e., the direction cosines of \vec{H} in the (c^*ab) reference system are (0,0,1), and $\theta_i^1 = \theta_i^2 = \theta_i^3 + \pi = \theta_i^4 + \pi$. (ii) when \vec{H} is applied in the plane perpendicular to the *b* axis; i.e., the direction cosines are (k,l,0), and $\theta_i^1 = \theta_i^2 + \pi = \theta_i^3$ $= \theta_i^4 + \pi$. Therefore, if Gd³⁺ ions occupy predominantly Ln^{3+} substitutional sites in the monazite-type orthophosphate single crystals, there will be one direction (the *b* axis) and one plane (the plane perpendicular to the *b* axis) of complete equivalence (i.e., only one seven-line spectrum will be observed).

The angular variations shown in Figs. 10 and 11 were obtained for LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ by rotating the magnetic field \vec{H} in the plane perpendicular to the b axis of the single crystals. The shaded face of the EuPO₄ crystal which contains the b axis (see Fig. 3) was attached to a Teflon wheel that was fixed to the bottom of a TE_{011} -mode K_a -band cylindrical cavity. The Teflon wheel was then turned in a vertical plane by means of a thin nylon string in order to orient the b axis of the crystal perpendicular to the horizontal plane of the external rotating magnetic field. Due to its peculiar habit (see Fig. 3), the LaPO₄ single crystal was directly fixed to the bottom of the cylindrical cavity with wax. The wax itself, which is frequently used in x-ray-diffraction experiments, was not inside the cavity, since it gives rise to parasitic signals. The LaPO₄ crystal was initially aligned with an x-ray diffractometer and then mounted in the EPR cavity. A small final adjustment could be made by slightly changing the inclination of the waveguide. Since the experimental angular variations show that the plane perpendicular to the b axis of the



FIG. 10. Angular dependence of the EPR transitions for Gd^{3+} in an LaPO₄ single crystal when \vec{H} is rotated in the plane perpendicular to the *b* axis [i.e., in the (010) plane]. Each curve in this figure is doubly degenerate, but due to a small misalignment of the LaPO₄ crystal, a slight resolution of the superimposed lines is apparent at certain angles. This proves that the (010) plane is a plane of equivalence for two magnetically inequivalent, but otherwise equivalent, Gd^{3+} sites. This result is in agreement with the symmetry properties of the four different *Ln* sites contained in the unit cell of the monazite structure (see Fig. 2) and with the occupation of predominantly Ln^{3+} sites by Gd^{3+} impurity ions.



FIG. 11. Angular dependence of the EPR lines of Gd^{3+} in a EuPO₄ single crystal when the applied magnetic field \vec{H} is rotated in a plane perpendicular to the *b* axis of the crystal [i.e., the (010) plane]. Each curve is doubly degenerate. The resolution of the superimposed lines which arises for certain angles due to a small misalignment of the crystal, is more evident for the $\pm \frac{7}{2} \leftrightarrow \pm \frac{5}{2}$ transitions.

crystals is effectively a plane of complete equivalence for the Gd^{3+} lines, it can be concluded that Gd^{3+} ions occupy predominantly Ln^{3+} substitutional sites. As can be seen in Figs. 10 and 11, however, all of the lines were not exactly superimposed, due to a small misalignment of the crystals.

In order to determine both the crystal-field parameters and the position of the principal electric field axes relative to the crystallographic axes, the following procedure was used:

(1) The monazite-structure crystal was fixed on the orienter described previously so that its b axis was parallel to the axis of rotation of the orienter. This axis lies in the horizontal plane, i.e., in the plane of the rotating external magnetic field.

(2) Both the orienter and the magnetic field were rotated in order to find an extreme of the position of the EPR lines for one of the two sets of magnetically equivalent Gd^{3+} ions, i.e., for sites (1) or (2). It should be noted that, during this procedure, the *b* axis remains in the horizontal plane. In the case of an absolute extreme, the *z* axis (z_1 or z_2) of one site is found. If a relative extreme is obtained, then it is denoted as the *y* axis (y_1 or y_2) according to the convention described in Sec. III.

(3) Without changing the position of the orienter, the magnetic field was then turned in the horizontal plane. In accordance with the crystal mounting orientation, this plane must still contain the *b* axis; and consistent with the 180° rotation along the *b* axis which transforms the (x_1,y_1,z_1) electric field axes into the (x_2,y_2,z_2) axes, it must also contain the other electric field axis for the other Gd^{3+} site. Therefore, the magnetic field \vec{H} can easily be turned from the $\vec{H} \parallel z_1$ extreme to $\vec{H} \parallel b$, where all of the Gd^{3+} ions are equivalent, to the $\vec{H} \parallel z_2$ extreme, and finally to $\vec{H} \perp b$, where again all of the Gd^{3+} ions are equivalent. Depending on the nature of the extreme (i.e., relative or absolute) the horizontal plane of the rotating magnetic field corresponds to the y plane, which is the plane containing y_1 , b, and y_2 , or the z plane, which contains z_1 , b, and z_2 . The angles θ_z or θ_y between the b axis and the electric field z or y axes were then directly determined by reading the angles at which the magnetic field was applied.

(4) Without turning the orientation device, the bottom of the cavity on which the orientation wheel is attached was then transported to an x-ray diffractometer, and a Laue-back-diffraction pattern was obtained with the x-ray beam oriented along the b axis (i.e., oriented perpendicular to the wheel). The angle between the horizontal plane, which corresponded to the z or y plane, and the crystallographic a axis could then be measured. It should be noted that some precautions were necessary, since the x-ray pattern gives the a^* and c^* axes of the reciprocal lattice, and not the a and c axes of the lattice. An identification of the a^* and c^* axes cannot be easily accomplished from a Laue-back-diffraction pattern, and therefore, these two axes were identified after removing the crystal from the orienter, using a precession camera. The EPR spectra for LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ presented in Figs. 12-15 have been obtained using this procedure. Since the b axis of the crystals was



FIG. 12. EPR spectra of a LaPO₄:Gd³⁺ single crystal with the magnetic field \vec{H} in the (z_1, z_2) plane. (a) The magnetic field \vec{H} is parallel to the principal electric field z axis of one of the two magnetically inequivalent sets of sites (1,4) or (2,3) (see Fig. 2). This axis has arbitrarily been called the z_1 axis. This does not necessarily mean that it is correlated with the sites (1,4). The almost equidistant EPR lines, which are identified at the top of the figure, correspond to the absolute extremes in the angular variation for the Gd³⁺ ions which are either in the (1,4) sites or the (2,3) sites, while the other lines in the center of the spectrum arise from the remaining two Gd³⁺ sites. (b) \vec{H} is parallel to the *b* axis of the monazite structure, and therefore all the Gd³⁺ sites are magnetically equivalent. Due to a small misalignment of the crystal, the EPR lines are not exactly superimposed. (c) \vec{H} is parallel to the *z* axis of the second set of sites, denoted here as the z_2 axis. The Gd³⁺ lines, which were in the center of the spectrum shown in (a), have now become the equidistant lines whose positions are labeled at the top of the figure. Note that the angle θ_z between z_1 and *b* is the same as the angle between z_2 and *b*, and is reported in Fig. 16 and Table III. (d) The magnetic field \vec{H} is perpendicular to the *b* axis, and again only seven doubly degenerate EPR lines are observed.





FIG. 13. EPR spectra of a LaPO₄:Gd³⁺ single crystal with the magnetic field \vec{H} in the (y_1, y_2) plane. (a) \vec{H} is parallel to one of the principal electric field y axes, arbitrarily called the y_1 axis here. The lines that are almost equidistant from the central $+\frac{1}{2} \rightarrow -\frac{1}{2}$ line correspond to the relative extremes and their positions are labeled at the top of the figure. (b) \vec{H} is parallel to the b axis of the monazite structure, and the two seven-line spectra are superimposed. (c) \vec{H} is parallel to the y axis of the other two sites, and consequently the lines which were in the central part of the spectrum in (a) are now at the relative-extreme positions indicated at the top of the figure. The angle θ_y between the y_1 and b axes or the y_2 and b axes is reported in Fig. 16 and Table III. (d) \vec{H} is perpendicular to the b axis, in the (y_1, y_2) plane, and again only seven doubly degenerate lines are observed. not exactly perpendicular to the Teflon wheel (a misalignment of 1° or 2° is frequently present), the lines do not coincide exactly at the position labeled $\vec{H} \parallel b$. It is remarkable that, for both LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺, the angle θ_z between the *b* axis and each of the electric field z axes is almost equal to the θ_{v} angle between the b axis and each of the electric field y axes. Therefore, for the sake of simplicity, the y and z axes have been drawn on the same cone in Fig. 16. The values of the θ_y and θ_z angles are reported in Table III, together with the values ϕ_y and ϕ_z , which determine the angles between the crystallographic a axis and the y or z plane, respectively. The labeling of the y axes $(y_1 \text{ or } y_2)$ and the z axes $(z_1 \text{ or }$ z_2) in Fig. 16 was established by calculating the angles between these electric field axes. As can be seen from Table III, the angles (y_1, z_1) or (y_2, z_2) are 90° within the experimental errors.

The correspondence between the z and v axes can then be obtained by simply measuring the angles between these electric field axes. The question of correlating one particular set of electric field axes with the corresponding crystallographic site (in fact the set of magnetically equivalent sites) is not simple, however. A model, such as Newman's superposition model,²⁰ should, in principle, be able to resolve this question. This model, however, has only been used for hosts which exhibit one main spin-Hamiltonian parameter (usually b_2^0). In this case, the prediction of b_2^0 from the nearest-neighbors position is relatively easy, since two free parameters (the power law exponent and the intrinsic parameter) can be adjusted. For Gd³⁺-doped monazite-type orthophosphates, the model must predict two spin-Hamiltonian parameters. b_2^0 and b_2^2 , with the same number of free parameters. Our preliminary calculations have indicated that this model is unable to predict simultaneously that the parameter b_2^0 is almost constant while the b_2^2 parame-

TABLE III. Angles characterizing the crystal-field principal axes of Gd^{3+} sites in monazite-type LaPO₄ and EuPO₄. Numbers in parentheses represent the estimated errors in the last place.

67°(2)
67°(2)
41°(4)
62°(4)
92°(5)



FIG. 14. EPR spectra of a EuPO₄:Gd³⁺ single crystal with the magnetic field \vec{H} in the (z_1, z_2) plane. (a) \vec{H} is parallel to one of the principal electric field z axes; i.e., the absolute extremes are found for one of the two sets of Gd³⁺ spectra. (b) \vec{H} is parallel to the *b* axis of the monazite structure; i.e., only seven doubly degenerate lines are observed. (c) \vec{H} is parallel to the *z* axis of the second set of sites, and (d) \vec{H} is perpendicular to the *b* axis; i.e., again only one spectrum consisting of seven lines is observed.

ter varies in these monazite-type orthophosphate hosts (see Table I). Therefore, it is not possible to unequivocally establish whether the set of electric field axes labeled (y_{1},z_{1}) in Fig. 16 is correlated with the sites (1,4) or with the sites (2,3) in Fig. 2.

The spin-Hamiltonian parameters deduced from measurements at the orientations $\vec{H} \parallel z$ and $\vec{H} \parallel y$ using single crystals are listed in Table II for the cases of LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺. These parameters were obtained by using the same method as that described for the powder spectra (see Sec. IV A) and are in good agreement with the powder spectra values given in Table I. The sign of b_2^0 was determined to be positive from intensity measurements for both crystals at K band (24 GHz) and 1.5 K. Surprisingly, this sign is different from that determined for the same parameter in the tetragonal orthophosphates, $LuPO_4$, YPO_4 , and $ScPO_4$.¹¹

C. $Ln PO_4$: Gd³⁺ single crystals

In the previous section, it has been shown that, in the first and last monazite-structure rare-earth orthophosphates, the Gd^{3+} ions are in the same substitutional Ln^{3+} sites, and that they are characterized by EPR spectra whose spin-Hamiltonian parameters



FIG. 15. EPR spectra of a EuPO₄:Gd³⁺ single crystal with the magnetic field \vec{H} in the (y_1, y_2) plane. (a) \vec{H} is parallel to the y_1 axis, (b) \vec{H} is parallel to the *b* axis of the structure, (c) \vec{H} is parallel to the y_2 axis, and (d) \vec{H} is perpendicular to the *b* axis. The lines which correspond to the relative extremes are labled at the top of the figure. Due to a small misalignment of the crystal, the lines are not exactly superimposed in the spectrum with $\vec{H} \parallel b$.

(Table II) and principal electric field axes (Table III and Fig. 16) are very similar. Therefore, the full analysis that was performed for LaPO₄:Gd³⁺ and EuPO₄:Gd³⁺ single crystals was not carried out for the other orthophosphate single crystals (i.e., for CePO₄, PrPO₄, NdPO₄, and SmPO₄). For the sake of com-



FIG. 16. Orientation of the principal crystal-field axes for Gd^{3+} in the monazite-type rare-earth orthophosphates. Since the angles θ_y and θ_z between the *b* axis of the structure and the *y* and *z* axes, respectively, are almost the same (see Table III), they are reported on the same cone. The angles θ_y and θ_z are directly measured from the EPR spectra shown in Figs. 12–15, while the ϕ_y and ϕ_z angles were determined from subsequent x-ray measurements.

pleteness, however, the EPR single-crystal spectra of Gd^{3+} in these four hosts are shown in Figs. 17–20. The crystals were oriented so that the magnetic field \vec{H} was parallel to the electric field z axis of one of the two sets of magnetically equivalent Gd^{3+} ions. The seven associated EPR lines for these Gd^{3+} ions are labeled at the bottom of the figures, and the additional lines are due to the other set of Gd^{3+} ions. The single-crystal line positions for $\vec{H} \parallel z$ are in good agreement with the corresponding EPR powder spectra shown in Figs. 4–9.

V. CONCLUSION

The cumulative results of EPR investigations of Gd^{3+} -doped monoclinic lanthanide orthophosphate single crystals and powders as described here provide the fundamental baseline data required for extended studies of the actinide ion Cm^{3+} . Trivalent curium is known to have an electronic configuration that is analogous to that of Gd^{3+} . Additionally, the present results have shown, not only that the Gd^{3+} probe ion occupies a lanthanide substitutional site in single-crystal specimens, but also that conversion of a mixed lanthanide oxide system to an orthophosphate form and precipitation from molten urea produces a compound in which the local environment of Gd^{3+} is unaltered. Accordingly, a chemical and physical pro-



FIG. 17. EPR spectrum of a CePO₄:Gd³⁺ single crystal when the magnetic field \vec{H} is applied parallel to the z axis of one of the two magnetically inequivalent sites. The lines that are almost equidistant from the central line are identified at the bottom of the figure and correspond to the absolute extremes. These occur at the same magnetic field positions as the z shoulders in Fig. 5.

cessing sequence similar to that required for the large scale production of orthophosphate solid bodies has not resulted in the production of nonstoichiometric material with complex impurity-defect centers. These results also indicated that the probe ion has not preferentially occupied an interstitial (or other) position in the monoclinic, monazite structure. The crystalline-electric-field splitting of the ${}^{8}S_{7/2}$ ground state of Gd³⁺ has been found to be relatively large in the monoclinic orthophosphate hosts investigated here. Accordingly, the corresponding EPR spectrum can be used as a sensitive indicator of deviations in the local environment of the Gd³⁺ "probe" ion. This sensitivity has already been used to detect



FIG. 18. EPR spectrum of a PrPO₄:Gd³⁺ single crystal when \vec{H} is parallel to the z axis of one of the two magnetically inequivalent sites. The lines labeled at the bottom of the figure, whose positions correspond to absolute extremes, are equivalent to the z shoulders of the corresponding powder spectrum (see Fig. 6).



FIG. 19. EPR spectrum of a NdPO₄:Gd³⁺ single crystal when \vec{H} is parallel to the z axis of one of the two magnetically inequivalent sites. The lines labeled at the bottom of the figure, which correspond to absolute extremes, occur at the same magnetic field positions as the z shoulders in the corresponding powder spectrum (see Fig. 7).

average random changes in the local crystal field produced by the incorporation of different concentrations of other ions identical to those found, for example, in commercial nuclear wastes.²¹ In an actual primary nuclear waste form, α -particle and α -recoil events will produce a significant amount of atomic displacement damage, and the sensitivity of the Gd³⁺ EPR spectrum to changes in the host lattice represents a potentially valuable means for studying radiation effects of this type. Again, the fundamental spectroscopic properties established in the present work form the basis for comparisons between unaltered and radiation-modified crystalline lanthanide orthophosphate systems.



FIG. 20. EPR spectrum of a SmPO₄:Gd³⁺ single crystal when \vec{H} is parallel to the z axis of one of the two magnetically inequivalent sites. The lines labeled at the bottom of the figure are found at the same positions as the z shoulders in Fig. 8.

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