The observation by EPR of trivalent hafnium in LuPO4, YPO4, and ScPO4

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The observation by EPR of trivalent hafnium in $LuPO_4$, YPO_4, and $ScPO_4$[a)]

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Recent EPR studies of the $4d^1$ configuration ion Zr^{3+} in the tetragonal-symmetry orthophosphate hosts $LuPO_4$, YPO_4, and $ScPO_4$, have led to additional investigations of d^1 configuration ions associated with unusual valence states of other elements. Single crystals of $LuPO_4$, YPO_4, and $ScPO_4$ doped with hafnium were grown and the electron paramagnetic resonance (EPR) spectrum of the $5d^1$ ion Hf^{3+} was observed in all three cases. EPR signals due to trivalent hafnium were only observed, however, when the doped samples were gamma irradiated at 77 K and maintained at 77 K during the EPR observations. Since there are two odd isotopes of hafnium with different nuclear spins and different natural abundances, identification of the spectrum of Hf^{3+} was straightforward. Since Hf^{3+} represents such an unusual valence for hafnium in the solid state, however, this identification was unequivocally verified by preparing crystals doped with isotopically enriched ^{179}Hf. The spectroscopic splitting factors, $g_{\parallel}$ and $g_{\perp}$, and the parallel magnetic hyperfine constants $A_{\parallel}$ of ^{177}Hf and ^{179}Hf were obtained for Hf^{3+} in all three hosts. A determination of the hyperfine parameters with the applied magnetic field oriented in the perpendicular direction was not carried out due to quadrupole effects. As in the case of Zr^{3+}, the observed electronic g values for Hf^{3+} could not be accounted for by the standard second-order equations which included the spin-orbit-induced admixture of some other excited orbital levels of the d^1 configuration into the ground orbital level. The ratio of the nuclear magnetic moments $^{177}\mu/^{179}\mu$, was determined to be 1.2361(4) and 1.2362(3) for hafnium in $ScPO_4$ and $LuPO_4$, respectively.

INTRODUCTION

Materials for the immobilization and long-term storage of radionuclides formed during nuclear reactor operation must satisfy a very restrictive set of criteria. For example, such substances must have the ability to chemically incorporate practical concentrations of radioactive elements without adverse alterations of their physical and chemical characteristics. They must be physically and chemically stable in the presence of high levels of γ and α particle radiation over very long time periods (10^5–10^6 yr) and must retain the incorporated radionuclides in the presence of ground waters with variable chemistry and under possible hydrothermal conditions.

The naturally occurring orthophosphate minerals monazite (a mixed rare-earth orthophosphate $LnPO_4$ where $Ln = La$, Ce, Pr, ...) and xenotime YPO_4 are known to have immobilized appreciable amounts of the radioactive elements thorium and uranium over geological time periods ($\sim 10^9$ yr). The established long-term stability of these orthophosphate minerals in the natural geologic environment has led to consideration of their application to the problem of nuclear waste disposal[1–3] and to a series of associated investigations of the solid state chemical and physical properties of these materials. These investigations have included electron paramagnetic resonance (EPR) studies of the valence states and site symmetries of iron group ($3d$), rare-earth ($4f$), and actinide ($5f$) impurities.[4–9] Other fundamental properties of the lanthanide and related orthophosphates have been deter-

mined using the techniques of x-ray diffraction,[10–12] Raman scattering,[13,14] optical absorption spectroscopy,[15,16] and Rutherford backscattering and other techniques.[3]

Orthophosphates of the first half of the lanthanide series (La–Gd) crystallize in the monoclinic monazite form, while orthophosphates of the second half of the series (Tb–Lu), as well as $ScPO_4$ and YPO_4 (xenotime) have the tetragonal zircon structure. Previous magnetic resonance studies of impurity ions in the tetragonal-symmetry orthophosphates have been particularly fruitful in that they have led to the observation of valence states of certain elements that are only rarely found in the solid state. For example, the $6s^1$ configuration ion Pb^{3+} was observed as a stable impurity in certain tetragonal orthophosphate crystals.[17] Additionally, the $4d^1$ configuration ion Zr^{3+} was found to exist as a stable species in $ScPO_4$ and $LuPO_4$ single crystals and as an unstable species (produced by γ irradiation at 77 K) in YPO_4.[18] In the present work, we extend these previous investigations of unusual paramagnetic valence states and report the successful observation by EPR of the $5d^1$ configuration ion Hf^{3+} in the single-crystal hosts $LuPO_4$, YPO_4, and $ScPO_4$.

EXPERIMENTAL

The orthophosphate crystals used in this study were grown by a flux technique that has been discussed in detail previously.[6] Both naturally abundant and isotopically enriched Hf dopants were used in the present work. The isotopically enriched Hf dopants (81.78% ^{179}Hf, 3.55% ^{177}Hf, and 14.67% even–even Hf) were obtained from the ORNL Isotope Sales Department in the form of the oxide HfO_2. Although all three crystals have the same type of tetragonal structure (i.e., the zircon structure) and exhibit {100} exter-

nal faces, the crystal habit of $ScPO_4$ (plate-like shape) is different from that of $LuPO_4$ and YPO_4, both of which grow in the form of long, thin bars.

A ^{60}Co γ source with a dose rate of $\sim 5 \times 10^5$ R/h was employed in the sample irradiations, which were carried out with the sample temperature maintained at 77 K. The irradiated samples were placed directly in a quartz flowing gas cold finger inside the microwave cavity of a conventional homodyne X-band EPR spectrometer without any intervening warmup. The spectrometer cavity (rectangular Varian V-4531 operating in the TE_{102} mode) and cold finger Dewar afforded a vertical sample entry hole, allowing a rapid change of samples to be made in order to maintain the irradiated samples at low temperature. This step was necessary because of the low thermal stability of the Hf^{3+} ions.

RESULTS AND DISCUSSION

EPR observations of the as-grown Hf-doped $LuPO_4$, YPO_4, and $ScPO_4$ crystals showed that the hafnium impurity had been incorporated in the nonparamagnetic tetravalent state in all three hosts. In each case, however, a short dose of ionizing radiation converted the hafnium to the trivalent state which was stable at 77 K but reverted to the tetravalent state upon warming the sample to room temperature. There are two naturally occurring odd isotopes of hafnium ^{177}Hf (18.5%, $I = 7/2$) and ^{179}Hf (13.75%, $I = 9/2$). These two odd isotopes combine to give a characteristic hyperfine structure in the EPR spectrum which provides a positive assignment of the observed spectra to hafnium in the three orthophosphate hosts and also permits measurements to be made of the ratio of the nuclear magnetic moments for the odd isotopes.

In the case of hafnium doped $ScPO_4$, the EPR spectrum shown in Fig. 1 was obtained at $T = 77$ K following a short dose of ionizing radiation at liquid nitrogen temperature (~ 15–30 min in a ^{60}Co gamma-ray source with $\sim 5 \times 10^{15}$ R/h). The observed EPR signals were sufficiently intense to permit a clear resolution and identification of the hyperfine lines due to the naturally occurring odd hafnium isotopes, ^{177}Hf ($I = 7/2$) and ^{179}Hf ($I = 9/2$). The intense central line shown in Fig. 1 is due to the $I = 0$ "even" isotopes of hafnium. The relative intensities of the hyperfine and central lines agree with the known natural abundances (18.5% ^{177}Hf, 13.75% ^{179}Hf, and 67.75% ^{even}Hf) and provide an identification of the Hf^{3+} spectrum. The spectrum in Fig. 1 was recorded with the applied magnetic field oriented parallel to the fourfold symmetry axis (i.e., c axis) of the $ScPO_4$ crystal. [There are three additional lines at low field in Fig. 1 which are part of the six line hyperfine spectrum of the $^{91}Zr^{3+}$ ion ($I = 5/2$) which is also present in this host.] When the applied magnetic field is not along the c axis, the selection rules break down due to the combined effect of the hyperfine, nuclear quadrupole, and nuclear Zeeman interactions. This effect, plus the interference of parasitic Zr^{3+} and Gd^{3+} resonances, produces a rather complicated spectrum and a detailed study of the complex hyperfine structure observed when the magnetic field is applied in the perpendicular direction was not deemed to be practical.
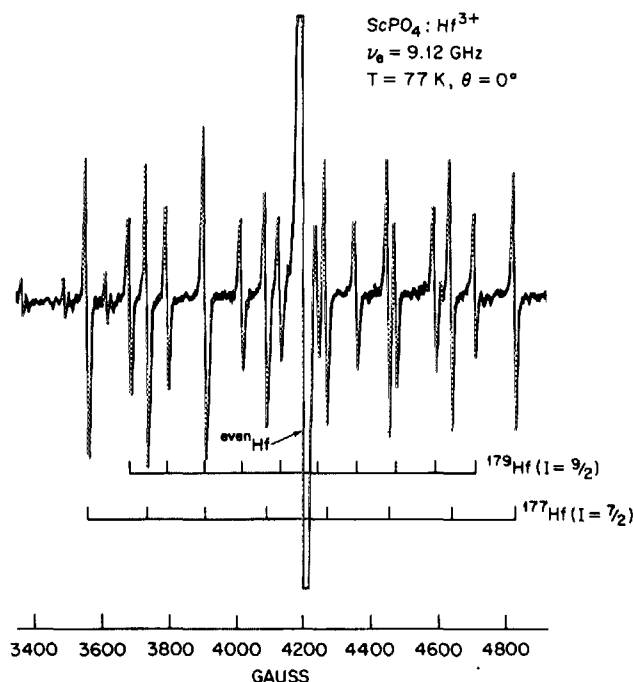

FIG. 1. EPR spectrum of naturally abundant Hf^{3+} in a single crystal of $ScPO_4$. The magnetic field is parallel to the c axis of the tetragonal crystal. The sample was irradiated with ^{60}Co gamma rays at 77 K and the spectrum was recorded at 77 K without any intervening warmup. The central line due to the even Hf isotopes ($I = 0$, abundance 67.75%) is flanked by one set of eight lines and another set of ten lines due to the ^{177}Hf ($I = 7/2$, abundance 18.5%) and ^{179}Hf ($I = 9/2$, abundance 13.75%) isotopes, respectively. The lines are labeled by the bar diagram below the spectrum. The additional three lines present at the low field side of the spectrum are hyperfine lines due to ^{91}Zr ($I = 5/2$).

The observed angular variation clearly establishes that there is only one Hf^{3+} site that is occupied in the unit cell (i.e., only one magnetic site) and that the Hf^{3+} spectrum exhibits a tetragonal symmetry variation about the crystal c axis. The spectroscopic parameters $g_\parallel$, $g_\perp$ $^{177}A_\parallel$ and $^{179}A_\parallel$ were obtained by fitting the usual axially symmetric spin Hamiltonian with $S = 1/2$, and these values are listed in Table I. From the total width of the hyperfine structure in the

TABLE I. Spin Hamiltonian parameters at 77 K for the d^1 configuration ions, Hf^{3+} and Zr^{3+}.

Trivalent hafnium				
	$g_\parallel$	$g_\perp$	$^{177}A_\parallel$ ($I = 7/2$)[a] (G)	$^{179}A_\parallel$ ($I = 9/2$)[a] (G)
$ScPO_4$	1.5504(1)	1.773 (1)	146.8 (4)	92.4 (3)
YPO_4	1.422 (1)	1.750 (1)	$\cdots$	110 (1)
$LuPO_4$	1.461 (1)	1.757 (1)	166.1 (4)	104.5 (3)
Trivalent zirconium[b]				
	$g_\parallel$	$g_\perp$	$^{91}A_\parallel$ ($I = 5/2$) (G)	$^{91}A_\perp$ ($I = 5/2$) (G)
$ScPO_4$	1.871 (1)	1.936 (1)	99.2 (2)	53.4 (1)
YPO_4	1.832 (1)	1.932 (1)	107.8 (2)	56.6 (1)
$LuPO_4$	1.844 (1)	1.933 (1)	105.4 (2)	55.7 (1)

[a] Note that for Hf^{3+} only the *parallel* hyperfine parameters for the isotopes ^{177}Hf and ^{179}Hf are reported.

[b] M. M. Abraham, L. A. Boatner, J. O. Ramey, and M. Rappaz, J. Chem. Phys. 81, 5362 (1984).
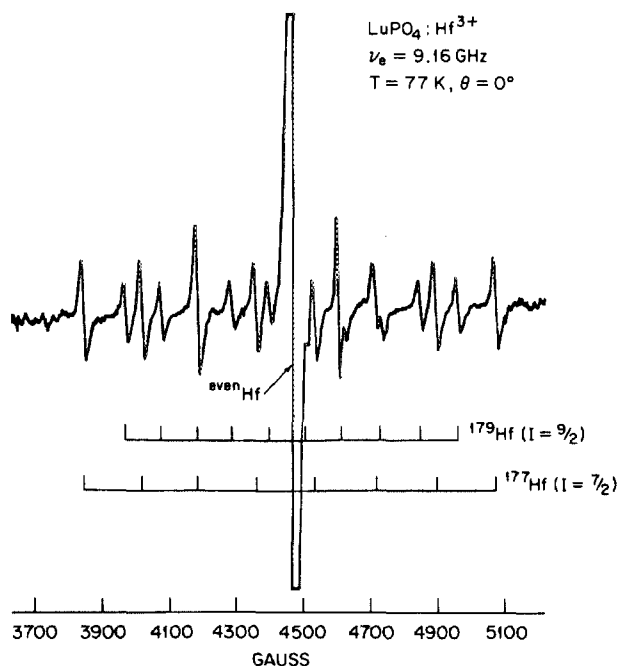
FIG. 2. EPR spectrum of naturally abundant Hf^{3+} at 77 K in a single crystal of $LuPO_4$ with the applied magnetic field parallel to the fourfold symmetry axis of the host crystal. The spectrum is produced following a gamma irradiation of the crystal at 77 K. The hyperfine lines due to the odd isotopes of Hf are labeled. An additional line, which appears on the seventh ^{179}Hf line (counting from low field), is due to a Gd^{3+} impurity.
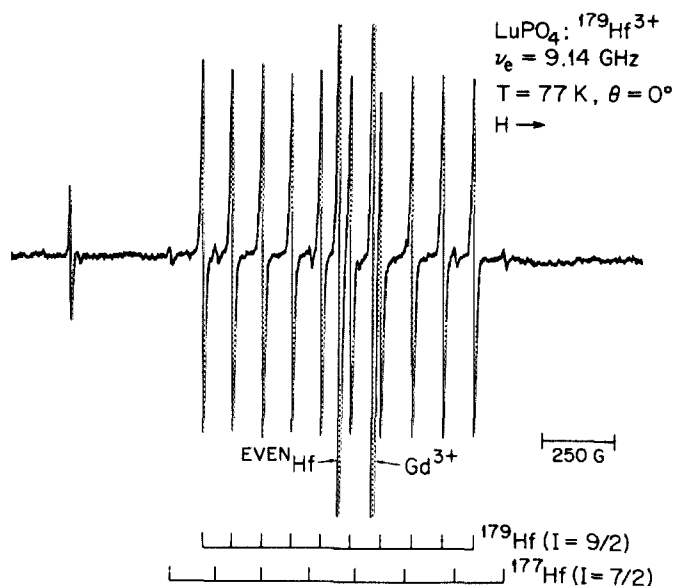

FIG. 3. EPR spectrum of isotopically enriched Hf^{3+} at 77 K in a single crystal of $LuPO_4$. The 81.78% abundance of ^{179}Hf increases the intensity of the ten ^{179}Hf lines relative to the eight ^{177}Hf lines and the central ^{even}Hf ($I = 0$) line. In addition to the Hf^{3+} absorption lines, resonance lines due to Gd^{3+} (labeled in the figure) and $^{even}Zr^{3+}$ (unlabeled at the low field side of the figure) are evident.

parallel magnetic field direction, we find for the nuclear magnetic moment ratio, $^{177}\mu/^{179}\mu = (7/9)$ $[^{177}A_{\parallel}/^{179}A_{\parallel}] = 1.2361(4)$ assuming no hyperfine anomaly. This ratio agrees very well with the ratio calculated from the reported values of the magnetic moments obtained using atomic beam techniques, $^{177}\mu/^{179}\mu = 0.7836(6)\mu_N/0.6329(13)\mu_N = 1.2381$.[19]

The EPR spectrum observed for naturally abundant Hf^{3+} in a single crystal of $LuPO_4$ following a low temperature (77 K) γ irradiation is shown in Fig. 2. The hyperfine structure for the odd Hf isotopes is again clearly evident and well resolved with the applied magnetic field oriented parallel to the tetragonal symmetry axis of the host crystal. The transitions are labeled by the bar diagram below the spectrum. There is an additional signal due to Gd^{3+} which is unlabeled and which is almost superimposed on the seventh (counting from low field) ^{179}Hf line in this orientation.

Single crystals of $LuPO_4$ doped with isotopically enriched ^{179}Hf (81.78% ^{179}Hf, 3.55% ^{177}Hf, and 14.67% ^{even}Hf) were grown and the resulting Hf^{3+} spectrum is shown in Fig. 3. The intensities of the ten ^{179}Hf hyperfine lines are obviously increased at the expense of the eight ^{177}Hf lines and the central ^{even}Hf line. In addition to the Hf^{3+} absorption lines, resonance lines due to Gd^{3+} (labeled in the figure) and $^{even}Zr^{3+}$ (unlabeled at the low field side of the figure) are observed. The narrower linewidths apparent in Fig. 3 as compared to Fig. 2 are exemplified by the better resolution evident between the seventh ^{179}Hf line and the Gd^{3+} line. With the magnetic field rotated from the c axis ($\theta = 0°$) toward the a axis ($\theta = 90°$) of the tetragonal $LuPO_4$ crystal, the situation regarding the Hf^{3+} hyperfine spectra

in $LuPO_4$ is the same as that found for $ScPO_4$, i.e., the central ^{even}Hf line exhibits the axial symmetry characteristic of the local substitutional site but the hyperfine structure becomes complicated primarily due to the relatively large quadrupole moments for the two odd hafnium isotopes.[20]

The spin Hamiltonian parameters determined for Hf^{3+} in $LuPO_4$ are given in Table I. The nuclear magnetic moment ratio obtained from the measured parallel hyperfine structure parameters $^{177}\mu/^{179}\mu = 1.2362(3)$, again, is consistent with the reported value determined by atomic beam techniques.[19]

EPR examinations of YPO_4 single crystals doped with naturally abundant Hf, indicated that the solubility limit of Hf in YPO_4 was lower than that characteristic of $ScPO_4$ and $LuPO_4$. Although a single line due to ^{even}Hf was observed in the EPR spectrum of YPO_4:Hf^{3+} following the required low temperature gamma irradiation, the spectrum could not be conclusively attributed to Hf^{3+} since, due to the low intensity of the central line, the characteristic hyperfine spectrum of the odd isotopes was not detectable. Accordingly, YPO_4 crystals doped with isotopically enriched Hf (81.78% ^{179}Hf, 3.55% ^{177}Hf, and 14.67% ^{even}Hf) were grown, and subsequent to the short gamma ray exposure at 77 K, the EPR spectrum illustrated in Fig 4 was obtained. The ten line hyperfine structure due to ^{179}Hf clearly identifies the spectrum of hafnium and establishes that the single central line belongs to the ^{even}Hf isotopes. In the spectrum shown in Fig. 4, however, the intensities of the eight ^{177}Hf hyperfine lines are too weak to be observed due to the ^{179}Hf isotopic enrichment. Other EPR transitions due to Pb^{3+}, Gd^{3+}, and $^{even}Zr^{3+}$ (unlabeled at the low field side of the figure) are also present in Fig. 4. As in the other host crystals, the Hf^{3+} spectrum in YPO_4 becomes increasingly complex on varying
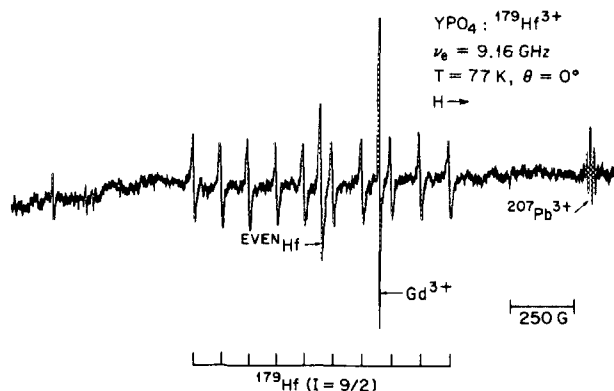
FIG. 4. EPR spectrum of isotopically enriched Hf^{3+} at 77 K in a single crystal of YPO$_4$. The spectrum, recorded with the magnetic field parallel to the fourfold symmetry c axis of the host crystal, exhibits ten hyperfine lines due to the enriched ^{179}Hf isotope flanking the ^{even}Hf central line. The signals of the ^{177}Hf isotope are too weak to be detected as a result of the isotopic enrichment. Absorption lines due to Pb^{3+}, Gd^{3+}, and ^{even}Zr^{3+} (unlabeled at low field side of the figure) are also present.

the applied magnetic field orientation from the $\theta = 0$ direction (the c axis orientation of Fig. 4) toward the $\theta = 90°$ direction (a axis). Therefore, only $g_\parallel$, $g_\perp$, and $^{179}A_\parallel$ were measured, and no attempt was made to carry out a detailed analysis of the competing interactions in the $\theta = 90°$ direction. It should be noted, however, that for all three host crystals, the magnetic hyperfine constants with the applied magnetic field along the perpendicular direction are smaller than the same parameters with the field applied along the parallel direction.

For a d^1 electronic configuration ion, a cubic crystal field will split the fivefold orbital degeneracy into an orbital doublet and an orbital triplet. The local symmetry in the tetragonal orthophosphates may be considered to arise from a tetragonal distortion of an eightfold-coordinated cubic-symmetry site. Therefore, the cubic-symmetry crystal field should result in a ground doublet level and an excited triplet level. Adding the tetragonal distortion, the ground doublet is split into two different orbital singlets, each of which retains a twofold spin degeneracy. This situation is precisely that described by Abragam and Pryce[21] and Bleaney et al.[22] for a d^9 ion in a crystal field resulting from a tetragonal distortion of a sixfold (octahedral) coordinated cubic crystal field with the proviso that the spin-orbit coupling constant is positive for a d^1 ion and negative for a d^9 ion. The spin-orbit interaction admixes a portion of the upper orbital triplet levels into the ground orbital singlet and changes the spectroscopic splitting factors, $g_\parallel$ and $g_\perp$, from the first order free-electron value, $g_e = 2.002\,32$. The experimental spin-Hamiltonian parameters listed in Table I for Hf^{3+} as well as the previously reported parameters for Zr^{3+} in the same three hosts where $g_\perp$ is also $> g_\parallel$ and $^{91}A_\parallel > {}^{91}A_\perp$ show that the orbital ground state is described by the symmetric wave function, $(1/\sqrt{2})\,[|+2> + |-2>]$ which transforms as $(x^2 - y^2)$. The matrix elements of the spin-orbit coupling connect the ground state only with states of the upper triplet; and, therefore, the departure of the two g values from the free-electron value may be expressed in terms of the spin-orbit coupling constant and the energy separations between the ground

singlet and one or the other of the two levels of the upper triplet (the latter is split into a singlet and a doublet by the tetragonal distortion). The experimental data both for the Hf^{3+} ion, as reported here, and the previously reported Zr^{3+} ion could not be reconciled with the theory of Abragam and Pryce[21,22] in order to obtain reasonable values of the two energy separations. There are obviously additional effects that must be taken into account in order to fit the observed g values. For example, Stevens[23] has noted that the assumption of the existence of a ^2D state in the crystal is an oversimplification and that overlap with the neighboring ions can lead to a diminution of the effective orbital magnetic moment.

SUMMARY

The resonance results show that there is only one magnetically equivalent hafnium site in the unit cell so that the observed EPR spectrum exhibits tetragonal symmetry about the crystal c axis. The angular variation of the Hf^{3+} clearly shows that the hafnium ion occupies a substitutional rare-earth site in the three hosts LuPO$_4$, YPO$_4$, and ScPO$_4$. A low temperature (77 K) γ irradiation was required for the production of the d^1 configuration ion Hf^{3+} in the three orthophosphate hosts. This valence state was not stable at room temperature and the ions reconverted to the initial tetravalent state between ~77 and ~297 K.

A comparison can be made between the stability of the trivalent state of hafnium in LuPO$_4$, YPO$_4$, and ScPO$_4$ and the stability of the $4d^1$ configuration ion Zr^{3+} in the same three host crystals.[18] While zirconium exists as a stable trivalent ion in both LuPO$_4$ and ScPO$_4$ and is observed in the as-grown crystals without any treatment by γ irradiation, Hf^{3+} can only be produced in LuPO$_4$, YPO$_4$, and ScPO$_4$ by irradiation at low temperature. The case of Hf^{3+} in the three orthophosphate hosts is similar to that of Zr^{3+} in YPO$_4$ where a low-temperature γ irradiation was required to produce the trivalent state and the Zr^{3+} ion reconverted to Zr^{4+} on warming to room temperature.

Since d^n configuration impurities are currently of interest as candidate systems for the development of new lasers, the stability of unusual valence states of these ions is of practical as well as fundamental importance. Questions regarding the relative stability of unusual valence states of ions such as Hf^{3+} and Zr^{3+} depending on the method of production (i.e., radiation-induced valence changes vs metal-vapor reduction, electrolytic reduction, etc.) have yet to be resolved. Most recently, attempts to produce trivalent titanium in the hosts LuPO$_4$, YPO$_4$, and ScPO$_4$ were successful and the results of EPR analyses of these systems will be presented at a later date.

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