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The occurrence and stability of trivalent zirconium in orthophosphate single crystals^{a)}

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EPR spectroscopy has been used in investigations of the unusual $3 +$ valence state of zirconium. The EPR spectrum of Zr^{3+} , which was initially observed as a parasitic signal in Fe-doped single crystals of $ScPO_4$, was definitively identified by preparing single crystals of $ScPO_4$ doped with isotopically enriched (94.6%) ^{91}Zr . Single crystals of $LuPO_4$ and YPO_4 doped with both naturally abundant and isotopically enriched Zr were also grown and investigated. The EPR spectrum of Zr^{3+} could be observed at room temperature in the "as-grown" single crystals of both $ScPO_4$ and $LuPO_4$; and, accordingly, the $3 +$ state is stable at room temperature in these hosts. The spectrum of Zr^{3+} in the YPO_4 host could only be observed following a γ irradiation at 77 K, and this spectrum decayed rapidly with increasing temperature. Axial spin-Hamiltonian parameters were determined for Zr^{3+} in all three hosts at a sample temperature of 77 K and at room temperature for the $ScPO_4$ and $LuPO_4$ hosts. In the case of the latter two hosts, the spin-Hamiltonian parameters were found to exhibit a small temperature dependence. The observed g values were not accounted for by previously published second-order expressions indicating that additional coupling mechanisms are operative.

INTRODUCTION

Polycrystalline ceramic materials based on mixed lanthanide orthophosphates represent promising hosts for the long-term disposal of high-level actinide and commercial nuclear reactor wastes.^{1,2} In the case of radioactive actinide wastes, geological evidence shows that naturally occurring mixed lanthanide orthophosphate minerals (i.e., monazites) have successfully contained both uranium and thorium for up to 10^9 years. Additionally, many of the actinides form orthophosphates whose crystal structure is the same as that of the lanthanide orthophosphates in the first half of the transition series, thereby creating a fortuitous match between the host waste form and the radioactive actinide species. In the case of high-level wastes resulting from the reprocessing of light water reactor spent fuel, a relatively high concentration of various lanthanides is present in the waste, and this material can be used as part of the basis for synthesizing the nuclear waste form itself.

Recognition of the interesting combination of characteristics exhibited by the lanthanide orthophosphates in the context of applications to the problem of nuclear waste disposal has stimulated general interest in the fundamental chemical and physical properties of these materials. The pure lanthanide orthophosphates are structurally divided into two classes: crystals formed from elements in the first half of the rare-earth series ($LaPO_4$ to $GdPO_4$) have the monoclinic "monazite" structure, while crystals formed from the second half of the series ($TbPO_4$ to $LuPO_4$, plus YPO_4 and $ScPO_4$) are characterized by the tetragonal "zircon" struc-

ture. Previous investigations of the solid state chemical properties of the two 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 resonance (EPR) spectroscopy.³⁻⁸ Additional studies have been carried out by means of x-ray diffraction,⁹⁻¹¹ Raman scattering,¹² optical absorption spectroscopy,¹³⁻¹⁵ and Rutherford backscattering and other techniques.¹⁶ In the present work, we report EPR observations of the unusual $3 +$ solid state valence of zirconium as an impurity in the tetragonal orthophosphate hosts $ScPO_4$, $LuPO_4$, and YPO_4 . Unequivocal identification of trivalent zirconium occupying substitutional metal sites in the three orthophosphate hosts was made by employing the highly enriched isotope ^{91}Zr .

In the case of Zr-doped $ScPO_4$ and $LuPO_4$ the trivalent state of zirconium was present in the as-grown crystals and, accordingly, exhibited long-term stability at room temperature—a somewhat unexpected finding. For zirconium-doped YPO_4 , the Zr^{3+} EPR spectrum was not observed in the as-grown crystals but could be produced by a short exposure to ionizing radiation at low temperature. In this case, however, the trivalent state was not stable at room temperature and a reversion to Zr^{4+} occurred on warming the YPO_4 sample to ambient temperature.

EXPERIMENTAL

The single crystals of the zircon-structure orthophosphates $LuPO_4$, YPO_4 , and $ScPO_4$ employed in this work were grown using a modified version of the flux technique previously described by Feigelson.¹⁷ The method for doping the single crystals with zirconium that eventually proved to be most successful consisted of the following procedure: The desired amount of Zr in the form of ZrO_2 (typically ~ 30 mg) was placed in a 50 cm³ platinum crucible, and a nonstoichio-

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metric amount of H_3PO_4 was added. The crucible was heated on a hot plate for 1 week at a temperature of $\sim 300^\circ\text{C}$. At this point, P_2O_5 was added and the crucible was heated with a torch to produce a dry powder. A final mixture consisting of this powder plus 3.5 g of R_2O_3 (where $\text{R} = \text{Lu}, \text{Y}, \text{Sc}$) and 60 g of PbHPO_4 was placed in the Pt crucible and covered with a tight fitting platinum lid. After heating the mixture at 1360°C for ~ 150 h in a muffle furnace, the solution was slowly cooled to 900°C at a rate of $\sim 1.0^\circ\text{C/h}$. At this temperature the growth run was terminated and the crucible was cooled to room temperature. The resulting crystals were removed from the solidified $\text{Pb}_2\text{P}_2\text{O}_7$ flux by boiling the crucible and its contents in hot concentrated nitric acid for about three weeks. Both naturally abundant and isotopically enriched Zr dopants were used in this study. The enriched samples of Zr [94.6% ^{91}Zr and 5.4% even-even Zr] were obtained from the ORNL Isotope Sales Department.

EPR investigations of the zirconium-doped orthophosphate single crystals grown as described above were carried out in the temperature range between ~ 77 K and room temperature by means of a conventional X-band spectrometer which employed a Varian TE₁₀₂ mode cavity and a 100 kHz modulation frequency. A proton magnetic resonance probe was used in measuring the applied magnetic field and both the microwave and proton resonance frequencies were determined using a Hewlett Packard HP-5245L frequency converter. The low temperature (77 K) sample irradiations were carried out in a ^{60}Co γ source (5×10^5 R/h).

RESULTS AND DISCUSSIONS

The EPR spectrum of what was eventually identified as trivalent zirconium was initially observed as a parasitic signal in iron-doped single crystals of ScPO_4 during the course of a series of investigations of Fe^{3+} in the three zircon-structure orthophosphates LuPO_4 , YPO_4 , and ScPO_4 .^{7,18} The observed spectrum was axially symmetric and clearly due to a substitutional impurity in a scandium site. It consisted of an intense central line flanked by six hyperfine lines attributable to an odd isotope with $I = 5/2$. This signal was classified as that of a d^1 electronic configuration ion but its identity was not definitely established at this point.

Since molybdenum has two odd isotopes, ^{95}Mo (natural abundance 15.8%) and ^{97}Mo (natural abundance 9.6%) both of which have a nuclear spin of $5/2$ and about the same value for their nuclear magnetic moment; and, because the d^1 configuration ion Mo^{5+} had been reported previously in a number of hosts, an initial cursory assignment of the spectrum to

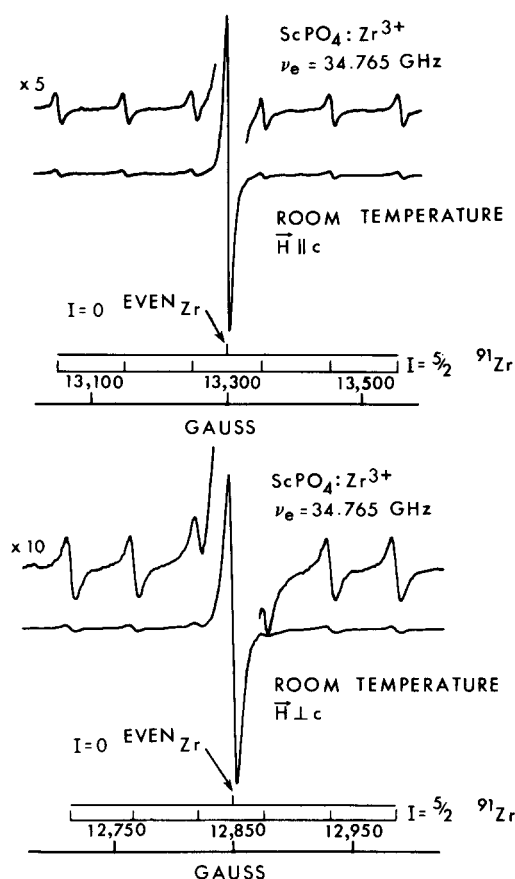


FIG. 1. EPR spectra of naturally abundant Zr^{3+} at room temperature in a single crystal of ScPO_4 . The top traces show the intense central even-even line at a g value of 1.867 with the applied magnetic field oriented along the fourfold symmetry axis of the crystal and the weaker six-line hyperfine pattern of the 11% abundant isotope ^{91}Zr . The hyperfine pattern is also shown enhanced by a factor of 5. The bottom trace shows the spectrum observed at a g value of 1.933 when the applied field is oriented perpendicular to the fourfold symmetry axis. The hyperfine pattern is also shown with a factor of 10 enhancement.

Mo^{5+} was made.⁷ A subsequent more detailed examination of this spectrum, including an integration and comparison of the hyperfine and central line intensities, showed that the total intensity of the six hyperfine lines as compared to the central line was, in fact, consistent with a value of only $\sim 11\%$ for the abundance of the odd isotope. This value was not consistent with the $\sim 25\%$ abundance of the combined odd Mo isotopes and more nearly coincided with the natural abundance expected for a zirconium impurity (Zr has one odd isotope ^{91}Zr with a natural abundance of 11.2% and $I = 5/2$).

Since a $3+$ zirconium valence state that is stable at room temperature represented a new and quite unexpected result, a series of investigations was initiated in order to obtain unequivocal identification of the origin of the parasitic EPR spectrum observed in ScPO_4 . New single crystals were prepared in the manner described earlier and were intentionally doped with either isotopically enriched ^{95}Mo or ^{91}Zr . No EPR signals attributable to Mo were observed in the ^{95}Mo -doped crystals. An EPR spectrum was observed in the enriched ^{91}Zr -doped crystals,¹⁹ however, and this spectrum was characterized by spin-Hamiltonian parameters that were identical to those determined from the spectrum of the

TABLE I. Spin-Hamiltonian parameters for Zr^{3+} .

	g	g	^{91}A (G)	^{91}A (G)	T (K)
ScPO_4	1.871(1)	1.936(1)	99.2(2)	53.4(1)	77
	1.867(1)	1.933(1)	98.9(4)	53.1(2)	295
YPO_4	1.832(1)	1.932(1)	107.8(2)	56.6(1)	77
LuPO_4	1.844(1)	1.933(1)	105.4(2)	55.7(1)	77
	1.842(1)	1.931(1)	105.1(4)	55.4(2)	295

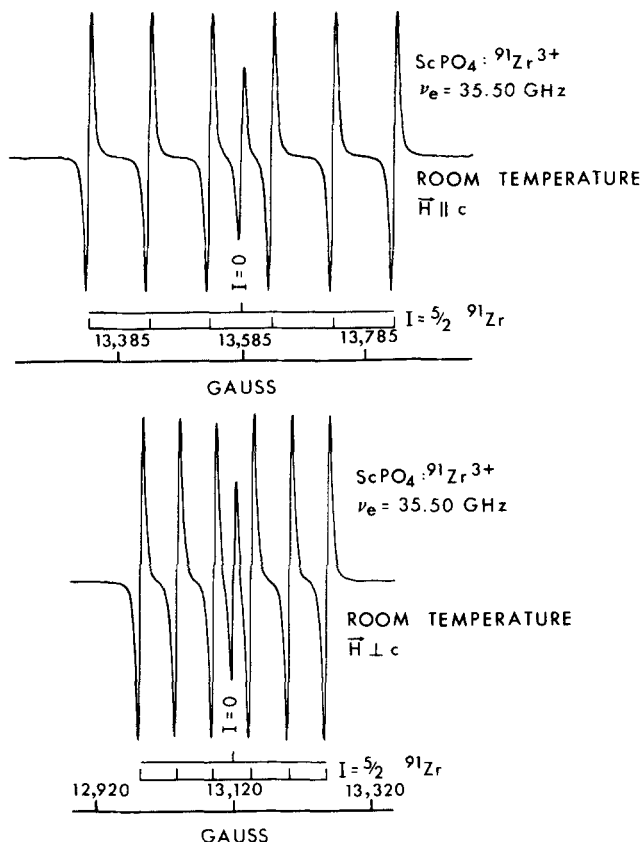


FIG. 2. EPR spectra of isotopically enriched zirconium (enriched to 94.6% ^{91}Zr) with the applied magnetic field parallel (top) and perpendicular (bottom) to the fourfold symmetry axis of the ScPO_4 host crystal. The weaker line at the center of the six-line hyperfine pattern is due to the residual even-even zirconium isotopes. These results establish that the spectrum is that of Zr^{3+} .

parasitic impurity (see Table I). The ratio of the intensities of the hyperfine and central even-even lines in the ^{91}Zr -enriched ScPO_4 crystal coincided with the known isotopic enrichment of the zirconium dopant. This proves conclusively that the d^1 configuration ion responsible for the observed EPR spectrum is trivalent zirconium.

The EPR spectrum observed for naturally abundant zirconium $3+$ in ScPO_4 is shown in Fig. 1 for the applied magnetic field oriented parallel and perpendicular to the fourfold symmetry axis of the ScPO_4 host. Traces with increased gain are also shown in Fig. 1 in order to clearly illustrate the six-line hyperfine pattern of the naturally abundant ^{91}Zr isotope. The corresponding spectra obtained using the highly enriched zirconium-91 isotope are shown in Fig. 2 for the magnetic field oriented along the two principal crystallographic directions. The line located at the center of the symmetric six-line hyperfine set in Fig. 2 is due to the transition associated with the even-even Zr isotopes. This transition is, of course, now reduced in intensity as a result of the enrichment.

The EPR spectrum of Zr^{3+} in ScPO_4 was characterized by an interesting temperature variation effect. When the temperature of the sample was lowered from room temperature to 77 K, it was found that the spin-Hamiltonian parameters describing the low-temperature spectrum differed sig-

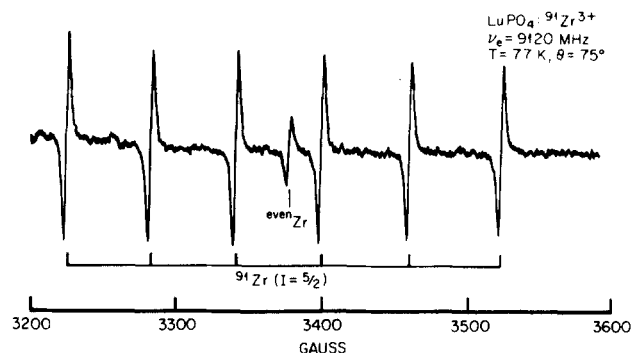


FIG. 3. EPR spectrum of isotopically enriched Zr^{3+} at 77 K in a single crystal of LuPO_4 with the applied magnetic field oriented at an angle of 75° relative to the fourfold symmetry axis of the host crystal. The LuPO_4 single crystals uniformly contained unwanted Gd^{3+} impurities and this orientation was chosen for the purposes of illustration to avoid interference from the Gd^{3+} EPR spectrum. Spin-Hamiltonian parameters for Zr^{3+} are listed in Table I for sample temperatures of 77 K and room temperature.

nificantly from the room temperature values, i.e., the g values are temperature dependent—at least in the range of 77 to 295 K.

Subsequent to the observation and definitive assignment of the EPR spectrum of Zr^{3+} in ScPO_4 , investigations of this ion in other related tetragonal-symmetry orthophosphates were initiated. Single crystals of LuPO_4 doped with the enriched zirconium-91 isotope and with naturally abundant Zr were grown. The EPR spectrum shown in Fig. 3 was observed for the ^{91}Zr -doped LuPO_4 sample. Unavoidable Gd^{3+} impurities were also present in the LuPO_4 single crystals and thus the Zr^{3+} spectrum in Fig. 3 is shown at an arbitrary angle of 75° in order to avoid confusion with transitions associated with the unwanted Gd^{3+} spectrum. The Zr^{3+} spectrum was observed at both room temperature and 77 K in the as-grown LuPO_4 crystals, and the spectroscopic parameters obtained by fitting the usual axially symmetric spin-Hamiltonian are listed in Table I. Again, it can be seen that the spin-Hamiltonian parameters for Zr^{3+} in LuPO_4 are temperature dependent in the region between 77 and 295 K.

Single crystals of YPO_4 doped with isotopically enriched ^{91}Zr were also prepared, but Zr^{3+} EPR signals could not be seen in the as-grown YPO_4 samples. The spectrum of Zr^{3+} was observed with a sample temperature of 77 K, however, following a short dose of ionizing radiation at liquid nitrogen temperature [~ 15 min in a ^{60}Co γ -ray source with $\sim 5 \times 10^5$ (R/h)]. The spectra obtained for enriched $^{91}\text{Zr}^{3+}$ in YPO_4 are shown in Fig. 4 for the applied magnetic field oriented parallel and perpendicular to the tetragonal symmetry axis of the host crystal. Again the residual spectrum from the remaining even-even Zr isotopes is apparent at the center of the six-line hyperfine set in Fig. 4. The spin-Hamiltonian parameters obtained by fitting the observed Zr^{3+} spectrum to the usual axial form are given in Table I. In the case of Zr-doped YPO_4 , the trivalent state of zirconium was not stable; and, upon warming, the spectrum decreased in intensity to the point that the spin-Hamiltonian parameters could not be obtained at room temperature. A heavier Zr doping, if it could be achieved, might permit the measurement of the room temperature parameters for the YPO_4

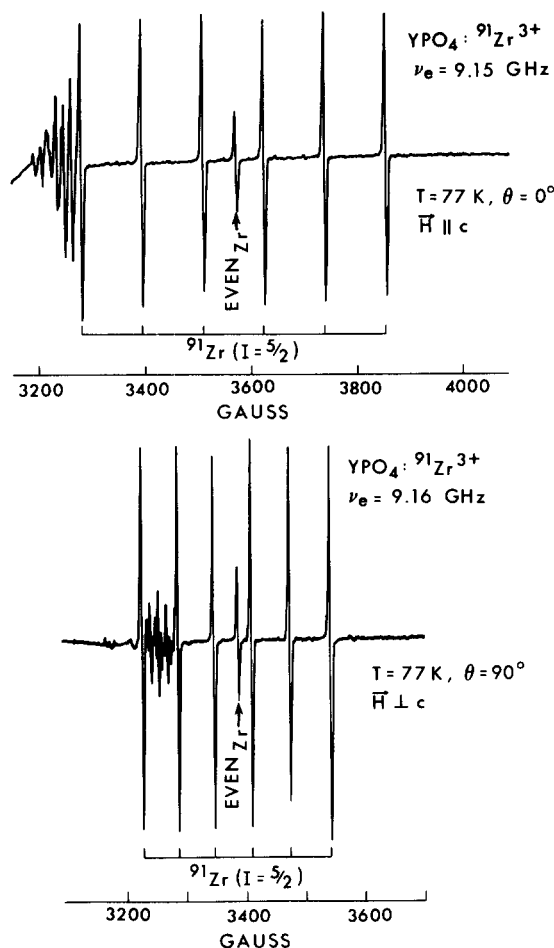


FIG. 4. EPR spectra of Zr^{3+} in YPO_4 at 77 K with the applied magnetic field parallel (top) and perpendicular (bottom) to the fourfold symmetry axis of the host crystal. In contrast to the spectra shown in Figs. 1–3 for the ScPO_4 and LuPO_4 hosts, the Zr^{3+} spectrum was not observed in the as-grown YPO_4 single crystals but was present following a gamma irradiation carried out at 77 K. This radiation induced Zr^{3+} spectrum decayed rapidly at room temperature. The additional complex structure apparent to the left of the lowest field ^{91}Zr hyperfine line in the top trace and between the first two (counting from low field) hyperfine lines in the bottom trace is due to the presence of a Pb^{3+} impurity (see Ref. 23).

host, since a very weak Zr^{3+} EPR spectrum was still observable in a 77 K γ -irradiated YPO_4 crystal after the crystal had been annealed for one day at room temperature.

While low-temperature γ irradiation was required to produce the $3+$ state for zirconium impurities in YPO_4 , it was found that, in fact, irradiation increased the trivalent zirconium concentration in the as-grown ScPO_4 and LuPO_4 hosts as well. These increased concentrations would rapidly reconvert to their original values, however, when the samples were warmed to room temperature. Accordingly, it is clear that there is some amount of tetravalent zirconium present in the as-grown hosts in all three cases. Some of the zirconium is already in a stable trivalent state in the case of the ScPO_4 or LuPO_4 hosts, but the γ irradiation converts a portion of the existing tetravalent zirconium into an unstable trivalent state for all three hosts.

A free ion with a d^1 electronic configuration such as Zr^{3+} has a fivefold orbital degeneracy. The crystal field of the zircon-structure orthophosphate hosts employed in the

present case can be considered as a superposition of an eight-fold cubic crystal field with an additional tetragonal distortion. The cubic crystal field splits the fivefold orbital degeneracy into a ground doublet level and an excited triplet level. With the additional tetragonal distortion, the ground orbital doublet is split into two orbital singlets. Either of these orbital singlets can be the ground state and the observed magnetic resonance spectrum is due to a transition between the two spin levels in the orbital singlet ground state. In the present case of Zr^{3+} in the orthophosphates, the fact that both the parallel and perpendicular g values differ from the free electron value implies that the orbital ground state is described by the symmetric wave function, $(1/\sqrt{2})[|+2\rangle + |-2\rangle]$, which transforms as $(x^2 - y^2)$.

The current situation for the orbital energy levels and states of the d^1 electronic configuration ion Zr^{3+} in an eight-fold coordinated site is the same as that described by Abragam and Bleaney²⁰ for a d^9 ion in a crystal field of octahedral symmetry with a tetragonal distortion. The g value for the ground orbital singlet which, to first order, is isotropic and equal to the free electron value, is affected by the spin-orbit coupling induced admixtures of the upper orbital triplet state and becomes anisotropic. Since the spin-orbit coupling constant is negative for a d^9 ion, the two principal g values become greater than two, whereas for a d^1 ion, the situation is reversed; i.e., the coupling constant is positive and the two g values are less than two. Attempts to fit the Zr^{3+} experimental data to the theory of Abragam and Pryce^{21,22} in order to calculate the energy separation between the orbital levels caused by the crystal field were not successful. This indicates that additional coupling interactions are operative and that the case of Zr^{3+} in the tetragonal orthophosphates does not fall within the limiting assumptions leading to the second-order expression given in Refs. 21 and 22. The observation that the Zr^{3+} spin-Hamiltonian parameters are temperature dependent also indicates that coupling to other electronic levels is important in this case.

Subsequent to the studies of both stable and γ -irradiation-induced Zr^{3+} reported here, an extension of this work was made in attempting to produce trivalent hafnium in the same three orthophosphate hosts. These attempts were successful and the results of the associated EPR spectroscopic studies will be reported elsewhere.

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