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ABSTRACT

Lanthanide orthophosphates formed from elements in the first half of the 4f transition series are analogs of the monoclinic mineral monazite. The known geologic properties of this mineral make the general class of lanthanide orthophosphate compounds attractive substances for long-term containment and disposal of α-active actinide nuclear wastes. EPR spectroscopy has been used to investigate the structural properties and solid state chemical properties of impurities in these materials and to compare the characteristics of single crystals and polycrystalline bodies.

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INTRODUCTION

The mineral monazite, a mixed lanthanide orthophosphate ($LnPO_4$ with Ln = La, Ce, Nd, ...), exhibits a number of characteristics that make analogs of this substance attractive as potential primary high-level radioactive waste forms [1,2]. These characteristics include an established long-term stability ($\sim 10^9$ years) under different geological conditions, a known ability to contain relatively high percentages of thorium and uranium, and an apparently high degree of resistance to metamictization due to α-particle and α-recoil radiation damage. This potentially important application of lanthanide orthophosphates has provided the impetus for a series of investigations of the physical and chemical properties of mixed orthophosphate-impurity systems. In particular, the technique of electron paramagnetic resonance (EPR) has been applied to the determination of valence states and site symmetries for various impurities in both single crystals and powders [3] of this class of compounds. In studying the solid state properties of mixed lanthanide orthophosphate-impurity systems, the EPR results have been correlated with investigations using optical techniques, Mössbauer spectroscopy, and x-ray diffraction. By using a probe ion whose spectrum reflects the properties of the crystalline electric field, it was also possible to obtain structural information by means of EPR spectroscopy.

Orthophosphates of the first half of the lanthanide transition series (i.e. La through Gd) crystallize in a monoclinic form that is the direct analog of natural monazite while the orthophosphates of the second half of the lanthanide series (i.e. Tb through Lu), as well as YPO_4 and $ScPO_4$, crystallize in a tetragonal form analogous to the mineral zircon. The EPR investigations were extended to encompass both lanthanide orthophosphate structural types.

EXPERIMENTAL

The lanthanide orthophosphate single crystals employed in these investigations were grown in a lead-based flux ($Pb_2P_2O_7$) using a variation of the technique described by Feigelson [4]. Following the growth by slow cooling, the crystals were removed from the entraining flux by boiling in nitric acid for about three weeks. Orthophosphate powder samples were prepared by a metathesis reaction using the appropriate lanthanide oxide and $(NH_4)_2HPO_4$, and were precipitated in molten urea [3].

The initial EPR studies concentrated on Gd^{3+} impurities in the monoclinic monazite-type orthophosphate hosts ($LnPO_4$ with Ln = La, Ce, Pr, Nd, Sm, Eu), and in the tetragonal zircon-type hosts $LuPO_4$, YPO_4, and $ScPO_4$. Fig. 1 shows the EPR spectra obtained for Gd^{3+} in $LuPO_4$. In this figure, the magnetic field is applied along the tetragonal c axis of the single crystal in the upper trace and along the a axis, i.e. perpendicular to the c axis, in the middle trace. The spectrum obtained for the corresponding powder is shown in the lower trace (i.e. Fig. 1c). It can be seen that the shoulders and divergences of the resultant powder pattern are in line with the single crystal transitions shown in the two traces above. These and similar investigations showed that the Gd^{3+} ion occupied identical substitutional sites in both the single crystal and powder specimens for either the monoclinic [5] or tetragonal systems [6]. In an actual waste, the material will undergo a series of chemical and physical processes which convert the waste oxides to the appropriate chemical form and compact this material into a high-density body. EPR spectroscopy provides a capability for verifying that following a complex processing sequence, the lanthanide or actinide impurities still occupy a known crystallographic site. The formation of potentially undesirable situations in which the α-active impurity is complexed with point defects introduced by a processing sequence (or eventually by radiation damage) or is converted to an interstitial position, can be detected. This represents an important capability for assuring predictable solid state chemical properties. It should be noted that this technique is applicable to all types of polycrystalline waste forms and is not simply limited to the lanthanide orthophosphates.

Prior to the investigation of radioactive actinide-doped orthophosphate samples, a systematic study of the isoelectronic rare-earth analogs was performed. Isotopically-enriched impurities were employed and EPR spectra of the Kramers' ions, Ce^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+} were observed in the tetragonal symmetry hosts $LuPO_4$, YPO_4, and $ScPO_4$. Unambiguous identifications of the various elements were facilitated by the use of the enriched isotopes and their corresponding characteristic hyperfine structures. The spectrum of Nd^{3+} was of particular interest since its electronic properties (i.e. $4f^3$ configuration) are analogous to those of trivalent uranium which has a $5f^3$ configuration. Therefore, an identification of the $^{238}U^{3+}$ EPR line was possible without the necessity of employing isotopically enriched uranium ^{233}U or ^{235}U. Fig. 2 shows the EPR spectrum obtained for a ^{145}Nd-doped single crystal of YPO_4 with the magnetic field along the tetragonal crystal axis. The spectrum was obtained at X-band and a temperature of 4.2 K. Additional lines due to Er^{3+} and Gd^{3+} are also present. Similar investigations of other lanthanide-actinide analog impurity systems are underway.

An unintentional Pb^{3+} impurity originating from the lead-based flux was observed in a substitutional cation site for the $LuPO_4$ and YPO_4 single crystals. A positive identification of Pb^{3+} (electronic configuration, $6s^1$) was made from the observation of the spectrum of the 20.8% naturally abundant isotope ^{207}Pb, which has a characteristically large hyperfine interaction. A five-line superhyperfine structure is evident in the EPR spectrum of even-even Pb^{3+} in YPO_4 as shown in Fig. 3. Electron nuclear double resonance (ENDOR) experiments at 4.2 K established that this structure is due to the four second nearest phosphorus neighbors surrounding the substitutional lead ion in the rare-earth site. At 4.2 K, each of the five principal superhyperfine lines in the EPR spectrum split into three components with intensities of 1:2:1, indicating an additional smaller interaction with two equivalent $I = 1/2$ neighbors. This smaller interaction arises from coupling to the two nearest ^{31}P nuclei. These results show that the s-electron wave function of Pb^{3+} is delocalized and its density is larger at the positions of the second-nearest ^{31}P neighbors than at the positions of the first-nearest neighbors.

A special set of circumstances made it possible to employ a new technique [7] in measuring the hyperfine constant of ^{207}Pb and the resulting values were the largest ever found for Pb^{3+} in a solid [> 48 GHz]. The solid state chemical restraints of the host lattice are apparently responsible for the conversion and stabilization of Pb^{2+} to Pb^{3+}. A similar situation occurs in the stabilization of divalent rare-earth ions in the alkaline earth halides. For the case of Pb^{3+} in $LuPO_4$ and YPO_4, no irradiation or electrochemical treatments were required for the $Pb^{2+} \rightarrow Pb^{3+}$ conversion and the trivalent ion was stable at room temperature.

Although lead is normally not a component of high-level radioactive wastes produced by nuclear reactor operations, it is an end member of certain branches of the decay schemes of the actinides. Therefore, after a sufficient period of time in the nuclear waste repository, lead will be a constituent of the primary waste form.

Real high-level nuclear reactor wastes contain many impurities in addition to the lanthanides and actinides. EPR spectroscopy can also be applied to the investigation of these other components that are paramagnetic. For example, the spectra of Fe^{3+} and Mn^{2+} have been observed in single crystals and powders of $LuPO_4$, YPO_4, and $ScPO_4$.

SUMMARY

The function of a crystalline substance in the role of a primary waste form is to incorporate or stabilize radioactive (and other) impurities in its crystal structure. The properties of such an impurity host ensemble can be determined, to a substantial degree, by the application of EPR spectroscopy. Here, lanthanide orthophosphates are being evaluated as waste forms for the containment of actinide and other elements. The currently available EPR results, combined with the results of Mössbauer and optical transmission spectroscopic studies, show that it is possible to incorporate 2+, 3+, 4+, and 5+ ions in the lanthanide orthophosphates. The ability to determine the valence states of various impurities and to obtain information regarding the location of ions in the host orthophosphate lattice represents an important capability in the evaluation of these materials as radioactive waste forms.

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FIGURE CAPTIONS

Figure 1. EPR spectra observed for Gd^{3+} in a single crystal (a), (b) and a powder (c) of $LuPO_4$. The applied magnetic field is oriented parallel to the 4-fold tetragonal symmetry axis in (a) and perpendicular to this axis in (b). In (c) the positions of the powder pattern shoulders are indicated by bars at the bottom of the figure and the divergences are marked by arrows.

Figure 2. EPR spectrum of $^{145}Nd^{3+}$ in YPO_4. Positions of the 8 ^{145}Nd ($I = 7/2$) hyperfine lines are indicated. The spectrum of naturally abundant Er^{3+} is also in evidence along with two Gd^{3+} fine structure lines.

Figure 3. EPR spectrum of the even-even isotopes of Pb^{3+} in YPO_4. The 5-line superhyperfine structure with a 1:4:6:4:1 intensity ratio is due to an interaction with four equivalent second nearest ^{31}P neighbors. The magnetic field is oriented parallel to the four-fold crystal axis. Additional transitions due to Fe^{3+} and Gd^{3+} are also evident.

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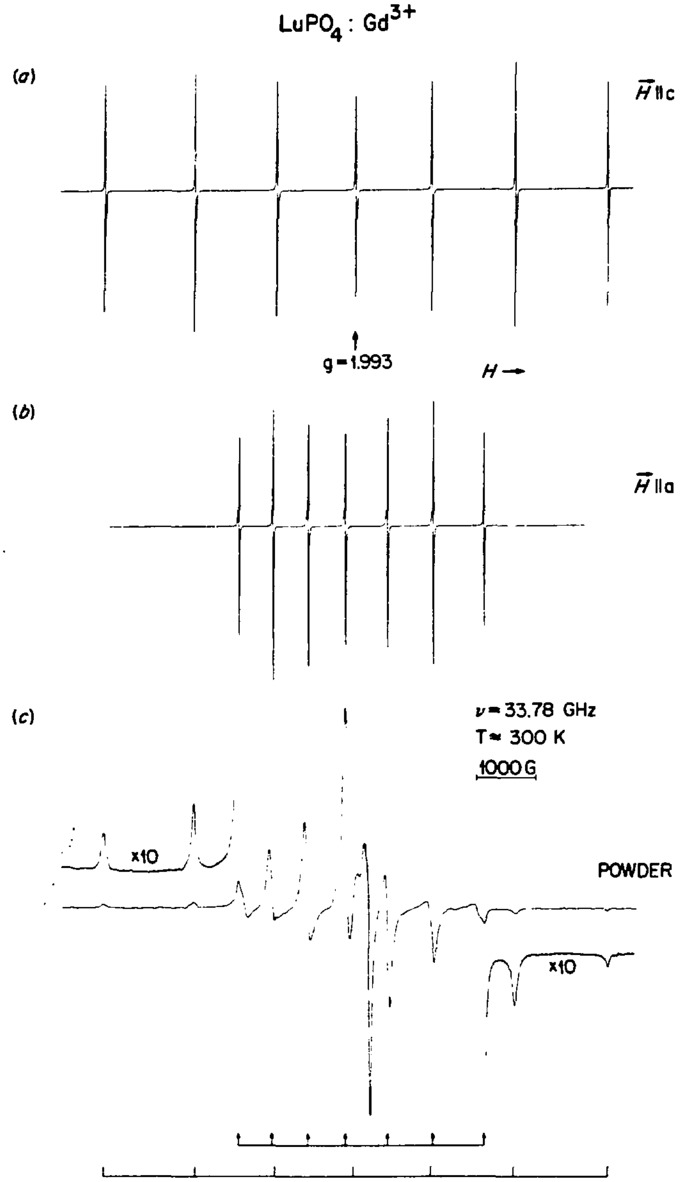

EPR SPECTRUM OF Gd^{3+} IN $LuPO_4$
(*a*) SINGLE CRYSTAL WITH $\vec{H}$ ∥ c
(*b*) SINGLE CRYSTAL WITH $\vec{H}$ ∥ a
(*c*) POWDER

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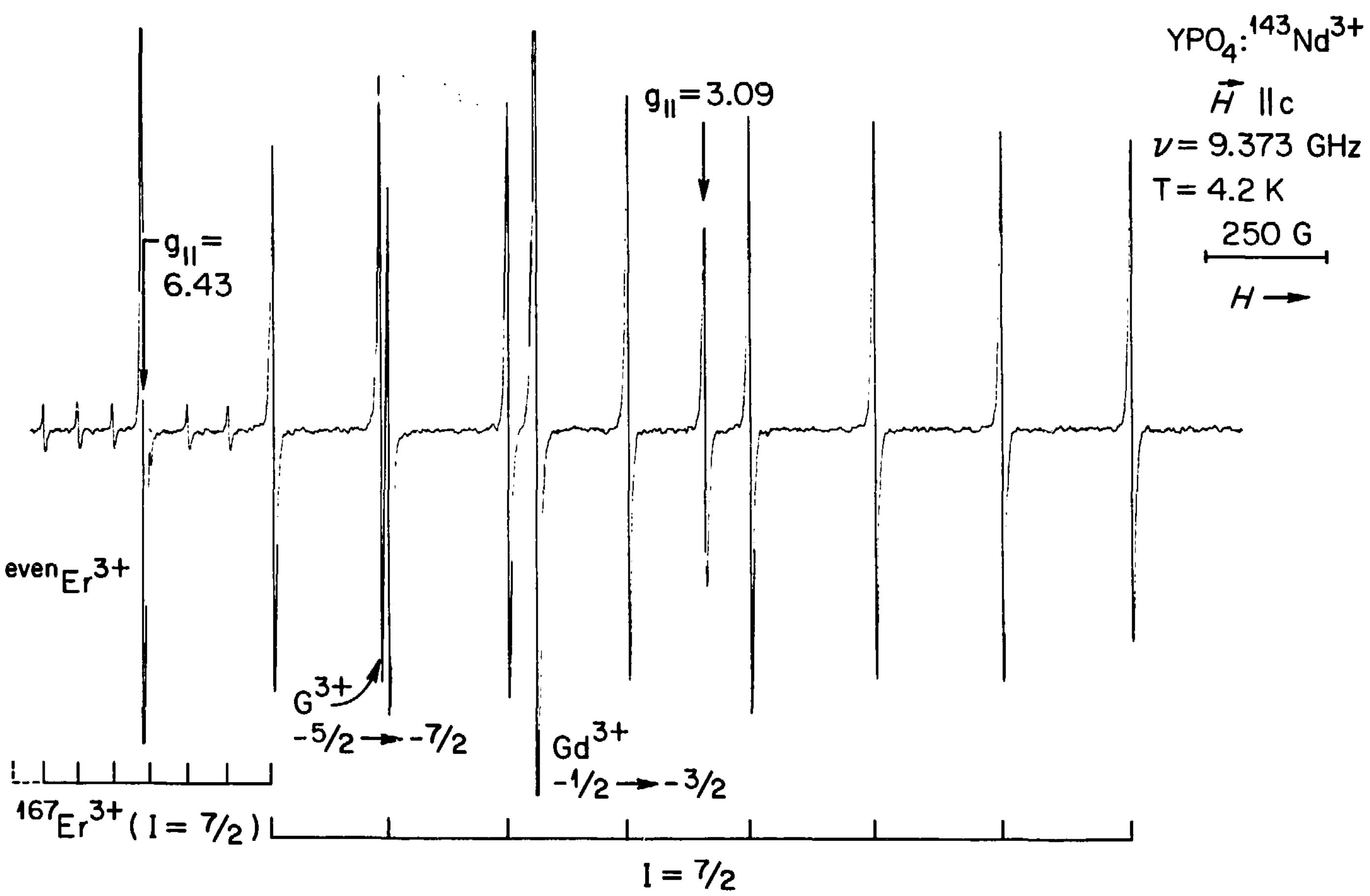

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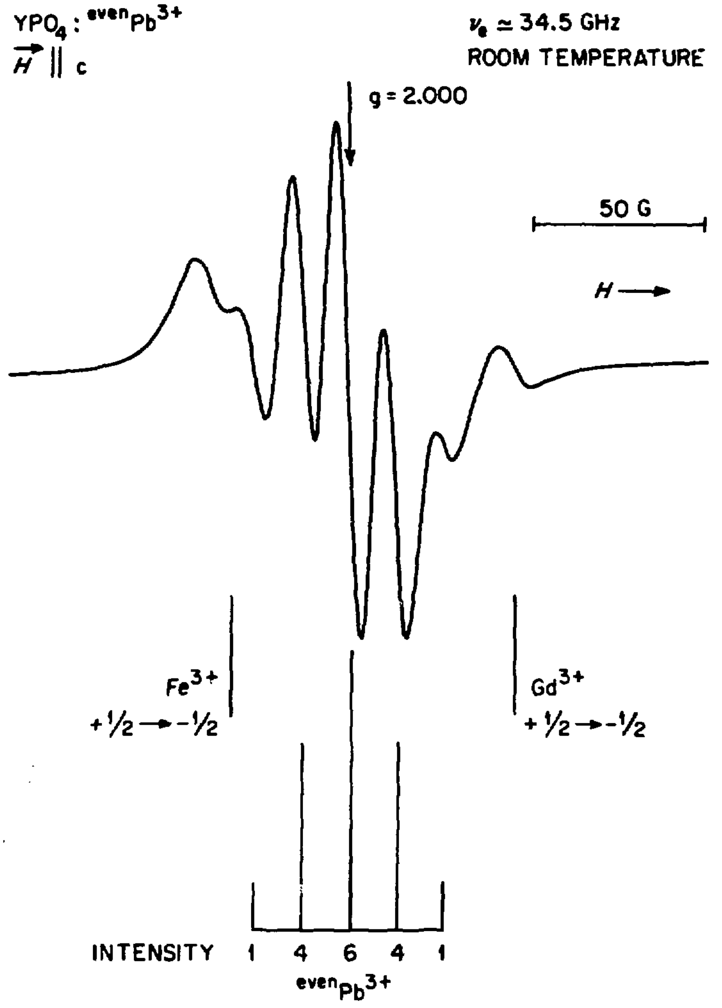

Pb^{3+} EPR Transition Exhibiting Superhyperfine Interactions with Four Equivalent ${}^{31}P$ ($I = 1/2$) Neighbors. The Magnetic Field $\vec{H}$ Is Applied Along the c-Axis of the YPO_4 Single-Crystal.