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INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy is one of the most powerful, site-specific techniques currently available for the study of certain types of impurities and defects in solids.¹ The technique is site-specific since the EPR spectrum can reflect the local environment (e.g., the crystalline electric-field symmetry and strength) of a paramagnetic ion or defect on a microscopic basis. In an approach to the containment and isolation of nuclear waste in which the primary waste form is a crystalline substance, the basic concept is to incorporate radioactive ions in an inert crystal lattice. Ideally, in such an incorporation, the radioactive ions will occupy substitutional sites in the lattice that are normally occupied by ions that constitute the inert crystalline host material. EPR spectroscopy yields the maximum amount of information when applied to exactly this type of solid-state situation (i.e., to paramagnetic impurities diluted in a crystalline substance). Accordingly, this technique can be extremely valuable in characterizing both ceramic waste forms and crystalline systems that are analogs of resistant natural minerals. Renewed interest in both of these types of alternative waste forms has recently been stimulated by findings relative to the stability of borosilicate glasses under certain hydrothermal conditions. It should be noted, however, that EPR spectroscopy has also been extensively applied to investigations of impurities and defects in glasses and, accordingly, its application to the problem of characterizing radioactive waste forms is not restricted to crystalline materials.

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Basically, EPR spectroscopy consists of the observation of magnetic dipole transitions (usually $\Delta M_s = \pm 1$) between electronic energy levels that are split by various perturbations. Most frequently, EPR deals with the electronic ground state of the paramagnetic impurity or center and an external magnetic field is usually applied in order to lift the ground state degeneracy. Transitions between the resulting magnetic-field-split Zeeman levels are then induced by photons whose frequency lies in the microwave region (e.g., 9 to 35 GHz for magnetic fields ranging between 3 and 12 kG). Since it is difficult to vary the microwave frequency in an EPR experiment, the energy difference corresponding to the various transitions is matched by varying the amplitude of the external magnetic field. Consequently, an EPR spectrum consists of one or more absorption lines whose number and magnetic-field positions will reflect: i) the type of impurity being studied, ii) the valence state of this impurity, and iii) the local crystal field symmetry at the impurity site. The type of information that can be obtained by means of EPR spectroscopy is summarized in Fig. 1. In addition to the information noted above, EPR can also be used to obtain quantitative analytical results as well as information concerning imperfections in the host material (e.g., radiation-induced defects and strains). In the following discussion, the types of information that can be obtained using EPR will be treated in more detail and specific examples will be presented.

Fig. 2 EPR spectra of ^{243}Cm , ^{244}Cm , and ^{241}Am in a single crystal of SrCl_2 .

IMPURITY IDENTIFICATION, VALENCE, AND SITE SYMMETRY

In its simplest, most direct application to the characterization of crystalline (or amorphous) waste forms. EPR spectroscopy can be used as a purely qualitative analytical tool for the identification of paramagnetic impurities or defects in solids. (A paramagnetic impurity or defect arises when the net orbital and spin angular momentum of the electronic system of such an entity is nonzero.) Nuclei that have an odd number of protons or neutrons (or both) are characterized by a nonzero nuclear spin I and an associated nuclear magnetic moment $\mu = g_N \beta_N I$ where g_N and β_N are respectively the nuclear g -value and nuclear magneton. In general coupling between this nuclear magnetic moment and the "electronic" magnetic moment of the paramagnetic ion results in a so-called "hyperfine" splitting or structure in the EPR spectrum. This hyperfine structure can often be used to make a positive identification of paramagnetic impurities. As an example, the EPR spectrum of the actinides ^{243}Cm , ^{244}Cm , and ^{241}Am in the fluorite structure host SrCl_2 is shown in Fig. 2.² For ^{243}Cm , the nuclear spin $I = 5/2$ so that $2I + 1 = 6$ hyperfine lines are observed; for ^{241}Am , $I = 5/2$ so that $2I + 1 = 6$ hyperfine lines are present in the spectrum of this isotope. The number of hyperfine lines, coupled with other spectroscopic information, can frequently be used to make a positive identification of impurities. In the case of naturally-abundant impurities, the intensity ratio between hyperfine lines of the various isotopes often provides a unique identification.

Fig. 3. EPR spectrum obtained using isotopically enriched ${}^{143}\text{Nd}$. Transitions due to Er^{3+} and Gd^{3+} are also present.

EPR spectroscopy can be used not only in determining that a given paramagnetic impurity is present but can provide an identification of its valence state. Such an identification can be made from the number of observed EPR transitions coupled with their position as a function of the strength of the applied magnetic field and its orientation relative to the axes of a host crystal. The utility of this approach for the identification of the valence states of impurities in solids can be enhanced by the ability to dope intentionally samples with isotopically enriched elements.

An example of an EPR spectrum in which the spectral complexity has been reduced by employing an enriched isotope is illustrated in Fig. 3. Here a single crystal of YPO_4 (xenotime) has been deliberately doped with the enriched isotope ${}^{145}\text{Nd}$. The characteristic 8-line hyperfine pattern coupled with the measured spectroscopic parameters can be used to identify the responsible ion as ${}^{145}\text{Nd}^{3+}$. The spectrum of Nd^{3+} is of particular interest since its electronic properties (it is characterized by a $4f^3$ electronic configuration) are analogous to those of trivalent uranium which has a $5f^3$ configuration. By investigating the spectroscopic properties of Nd^{3+} it is possible to identify and investigate impurities of ${}^{238}\text{U}$ and avoid the

Table 1. PW-4b Composition and Valence States

	MOL %	VALENCE	DETECTED BY EPR		MOL %	VALENCE	DETECTED BY EPR
La	26.4	+3	+2	Pd	4.1	+2, +4	+3
Ce		+3, +4	+3	Sr	3.5	+2	
Pr		+3, +4	+3	Ba	3.5	+2	
Nd		+3	+3, +4	Rb	1.3	+1	
Pm		+3	+3	U	1.4	+3, +6	+3, +4, +5
Sm		+2, +3	+3	Th		+4	
Eu		+2, +3	+2	Np	0.2	+3, +6	+4, +6
Gd		+3	+3	Pu		+3, +6	+3, +6
Tb		+3, +4	+3, +4	Am		+3, +6	+2, +4
Dy		+3	+3	Cm		+3	+3
Ho		+3	+2, +3	Fe	6.4	+2, +3	+1, +2, +3
Er		+3	+3	Na	1.0	+1	
Tm	13.2	+2, +3	+2	PO ₄	3.2		
Yb		+2, +3	+3	Tc		+7	+4
Lu		+3		Rh		+2, +3, +4	+2
Zr		+4		Te	9.0	+2, +4, +6	
Mo		+6, +2	+3, +5	In		+3	+2
Ru		+2, +3, +4	+3	Ni		+2, +3	+1, +2, +3
		+6, +8		Cr		+2, +3, +6	+3, +5 (+4) +1 (+2)
Cs	7.0	+1					

necessity of employing the radioactive uranium isotopes ^{238}U or ^{235}U . It should be noted that EPR transitions due to Gd^{3+} and Er^{3+} (naturally abundant) are also present in the spectrum shown in Fig. 3.

From Table 1, it is apparent that EPR spectra have been observed for most of the elements that are present in the composition of PW-4b nuclear waste. The second column of Table 1 lists the chemical valence states usually found for these elements in accordance with the periodic table. The third column lists the valence states for which an EPR spectrum has been reported in the literature. For special cases such as La^{2+} , unusual valences induced by the crystal host and/or irradiation have been observed by EPR.

Lanthanide orthophosphate compounds (i.e., analogues of the mineral MONAZITE) are currently being investigated as a potential primary waste form (or a waste-form phase) for the isolation of actinide and other radioactive isotopes.^{3,4} Flux-grown single crystals of these substances have been intentionally doped with rare-earth, actinide, and iron group impurities and EPR spectroscopy (supplemented by optical and Mössbauer studies) was used in identifying the valence of various impurity ions in the solid state. These investigations have shown that it is possible to incorporate divalent, trivalent, tetravalent, and pentavalent ions from the actinide, lanthanide, and iron groups in the lanthanide orthophosphates.

Fig. 4. Angular variation of the EPR transitions of Gd^{3+} in $LaPO_4$ illustrating the spectral symmetry properties.

It should be noted that the valence state of a paramagnetic impurity can also frequently be determined using a polycrystalline sample (e.g., a powder or solid ceramic body), and it is often not necessary to use a macroscopic single crystal specimen.

When a free ion, whose electronic wavefunctions are of the form $|LSJM_J\rangle$, is placed in a host lattice it experiences a crystalline electric field due to the surrounding ions of the lattice. This electric field generally removes the $2J+1$ degeneracy of the free-ion energy levels. The number of multiplets resulting from this interaction depends on the symmetry of the crystalline electric field and, therefore, the symmetry properties of an EPR spectrum can reflect those of the surrounding crystal field. An example of this type of dependence is shown in Fig. 4 where the angular variation of the spectrum of Gd^{3+} in $LaPO_4$ is plotted.⁵ For the case of the lanthanide orthophosphates, EPR spectroscopic studies of Gd^{3+} were used to show that each unit cell of $LaPO_4$ contains two magnetically inequivalent, but otherwise equivalent, lanthanum sites. The amount by which the free-ion energy levels are split is, of course, related to the strength of the crystalline electric field and this field strength is also often manifested in the properties of an EPR spectrum. A dependence of the paramagnetic-resonance spectrum on the local crystal-field-symmetry and strength can be used to obtain information

pertaining to the local crystal structure and to detect the possible formation of complex associated defects arising, for example, from deviations from stoichiometry or radiation effects.^{6,7}

EPR spectroscopy can provide useful information via the line intensity which is proportional to the number of paramagnetic impurities. Therefore, some indication of the nature of the phase diagram can be obtained for mixed host-impurity systems. Quantitative analytical results obtained using EPR are, however, often not as accurate as those available from other techniques.

01 = 02 = 1 = working size
 01 = -7 pieces final size

and the EPR spectra of Gd^{3+} in these samples have been compared with that obtained for a pure $LaPO_4$ single crystal. Figure 5 shows quantitatively the relationship between the average linewidth of two symmetric EPR transitions and their magnetic field separation for pure and PW-4b doped $LaPO_4$ crystals. These measurements were carried out for four different crystals and two different magnetic field orientations. Since the linewidth of each transition is proportional to its magnetic field separation from the central line, it can be concluded that the line broadening is "inhomogeneous" (i.e., the line broadening is due to a distribution of line positions with this distribution resulting from a distribution of impurities in the crystal).

The sensitivity of Gd^{3+} linewidths to defects or strains is also under investigation as a means of detecting metamictization phenomena in orthophosphates. Mixed $Ln_{1-x}An_xPO_4$ crystals, where Ln is a rare earth and An an actinide, have been grown and EPR spectra of Gd^{3+} in these systems are of considerable interest for detecting radiation damage created by α -particles or recoil of the daughter nuclei.

CONCLUSION

Although the examples of the application of EPR to waste form characterization described here have emphasized studies of lanthanide orthophosphates, the same techniques can be applied to perovskite, hollandite, zirconolite, etc. single crystals or powders or to amorphous materials.

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