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Electron Paramagnetic Resonance Spectra of Er(III), Dy(III), and Gd(III) in Yttrium and Lanthanum Hydrides

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Introduction

Many lanthanide, actinide, and transition elements form binary hydrides that are metallic in appearance, have metallic conductivities, and show other metallic properties such as ordering at low temperature. Substantial regions of nonstoichiometry and transition to semimetallic behavior as the trihydride composition is approached also characterize these materials. Yttrium and lanthanum typify lanthanide behavior by combining with hydrogen at moderate temperatures and low hydrogen pressures to approach a cubic fluorite structure for the dihydride with the hydrogen atoms occupying tetrahedral sites in the cubic metal lattice. Recent neutron diffraction results for YH_x confirm earlier neutron diffraction studies for analogous Ce, La, and Pr compounds as well as optical studies for YH_2, ScH_2, and LuH_2 that suggest filling of octahedral sites begins well before the dihydride composition, which would ideally have only tetrahedral sites occupied, is reached. Further addition

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of hydrogen to lanthanum (or Ce, Pr, Ne) retains the cubic metal arrangement continuously as the octahedral sites are filled and the stoichiometry approaches that of the trihydride, while yttrium (or Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) forms a hexagonal trihydride with slightly distorted tetrahedral and much more distorted octahedral sites.\(^1\)

Simple bonding theories for these metallic hydrides have treated the hydrogens as atoms in a metallic lattice, as H\(^+\) ions with the valence electron added to the conduction band, or as H\(^-\) ions with an electron withdrawn from the conduction band.\(^1\) That the lanthanide metal has transferred three electrons to the conduction band and can be considered a trivalent ion is generally accepted on the basis of magnetic data. Until recently, some controversy existed as to the relative merits of the protonic and hydridic models for hydrogen. Recent Mössbauer data\(^7-10\) for Dy, Er, and Gd, both as pure dihydrides and diluted in YH\(_2\), support the hydridic model, as do self-consistent band calculations\(^6\) that indicate a shift of electron density away from the metal atom and toward the hydrogen.

The present study was undertaken to confirm the oxidation state of the metal and the hydridic nature of the hydrogen by obtaining electron paramagnetic resonance (EPR) parameters sensitive to the oxidation state of the metal and to the sign of the charge on the hydrogen for representative lanthanides (Er, Dy, and Gd) diluted in the nonmagnetic host materials YH\(_x\) and LaH\(_x\). For hydride compositions near \(x = 2.0\), the environment of the dopant metal ion should be cubic for the majority of the ions present, thus providing a convenient
situation for determining the oxidation state and electronic ground state of the ion in question so as to distinguish between protonic and hydridic crystalline electric fields.

By the treatment of Lea, Leask, and Wolf,\textsuperscript{11} Dy\textsuperscript{3+} in a cubic crystal field should have either a $\Gamma_7$ ground state to give an isotropic EPR transition at $g = 7.56$, or an anisotropic $\Gamma_8$ ground state. Similarly, Er\textsuperscript{3+} in a cubic crystal field yields a $\Gamma_7$ ground state with an isotropic transition at $g = 6.80$, or a $\Gamma_6$ ground state with an isotropic transition at $g = 6.00$. Gd\textsuperscript{3+}, with an $^8S_{7/2}$ ground state, should have an isotropic transition in a cubic field at $g = 2.00$, although with a large zero-field splitting such as is seen for Gd\textsuperscript{3+} doped into CaF\textsubscript{2}.\textsuperscript{12} Crystal fields of lower symmetry as in YH\textsubscript{3}, should produce anisotropic EPR transitions and correspondingly more complex spectra. For the cubic case, a $\Gamma_7$ ground state for both Er\textsuperscript{3+} and Dy\textsuperscript{3+} is consistent with the hydridic point charge model.\textsuperscript{7,9,10} Similar arguments may be used to predict the ground states for other lanthanide ions in cubic crystal fields.\textsuperscript{11}

After this work was completed, we discovered that Venturini and coworkers\textsuperscript{13-17} have applied the EPR technique to determine the local site symmetries of dilute Er in group IIIB and IVB metal hydrides.

**Experimental Section**

Metal alloys were made by arc melting weighed amounts of the host and dopant metals. Nominal dopant concentrations were confirmed (within a factor of 2) for several alloys by x-ray fluorescence. Alloy samples were first held at 600°C for 30 minutes under vacuum,
then maintained at 600°C and 200 torr hydrogen pressure until no further hydrogen uptake was observed (typically 2 hours), and finally quenched to room temperature rapidly by removing the furnace. This procedure produced YH$_2$ whose composition was confirmed by its x-ray powder pattern, although precise stoichiometry was not established since the x-ray lattice parameter is insensitive to stoichiometry within the dihydride phase region.$^{18}$ LaH$_2$ was produced similarly, but with 20 torr of hydrogen. YH$_3$ and LaH$_x$ with $x > 2$ were produced by heating the alloy to 600°C in vacuum, adding H$_2$ to 700 torr and maintaining that pressure and temperature overnight, then cooling slowly to room temperature. X-ray powder patterns were used to confirm the YH$_3$ phase and to establish the actual stoichiometry of the LaH$_x$ since the lattice parameter for LaH$_x$ varies significantly with composition.$^{19}$ X-band EPR spectra were recorded with the samples in flowing helium gas at a temperature of ~100K. Samples of YH$_2$ and YH$_3$ doped with Yb, Sm, Eu, and Ce failed to give observable signals. However the cerium samples were particularly sensitive to air oxidation and formed some oxide prior to arc melting so the hydride samples may not have contained significant amounts of Ce.

**Results and Discussion**

The EPR spectra summarized in Table I are characteristic of the trivalent ions of Er, Dy, and Gd, thus confirming the +3 oxidation state for the metal ions with three electrons presumably donated to the conduction band in the dihydrides. Sm$^{3+}$, with a $^1$G$_8$ ground
state in a cubic hydridic crystal field, should have an anisotropic EPR transition so that failure to observe spectra for samarium is consistent with the +3 state. Europium might be expected to remain Eu\(^{2+}\) with an easily observable isotropic \(^8S_{7/2}\) ground state since pure EuH\(_2\) cannot be converted to a higher hydride,\(^1\) so failure to observe spectra for samples doped with europium is consistent with Eu\(^{3+}\) in YH\(_x\). Ytterbium, which could be expected to exhibit an isotropic \(\Gamma_7\) ground state if present as Yb\(^{3+}\), apparently remains in the diamagnetic \(+2\) state as it does in pure orthorhombic YbH\(_2\) since spectra are not observed for Yb in this cubic host. Preliminary studies of pure YbH\(_2\), however, did give EPR transitions at \(g = 4.7\) and 3.9 perhaps indicating some Yb\(^{3+}\) in this lower symmetry environment as has been suggested\(^1\) to explain the slight room temperature paramagnetism of YbH\(_2\).

In the cubic environment of YH\(_2\), Er\(^{3+}\) and Dy\(^{3+}\) both exhibit isotropic g values characteristic of a \(\Gamma_7\) state consistent with the hydridic point charge model and not with the protonic point charge model for the crystal field.\(^7\)-\(^10\) The g value for Er of 6.60 ± .05 in YH\(_2\) is lowered only slightly from the value of 6.77 predicted for a \(\Gamma_7\) ground state and the value 6.778 ± 0.003 measured by Venturini\(^{14}\) for Er\(^{3+}\) in YH\(_{1.99}\) at 2°K. The difference in the measured g values is due to the measurements being done at different temperatures. The observed g value of 6.9 for Dy in YH\(_2\) is somewhat further lowered from the predicted value of 7.56 for a
$^7$ ground state, presumably due to the temperature dependence of the conduction electron coupling.\textsuperscript{20,21} As the symmetry of the crystal field is reduced upon going from YH$_2$ to YH$_3$, the powder spectra of Er$^{3+}$ and Dy$^{3+}$ become considerably more complex. The $g$ values for Er$^{3+}$: YH$_3$ reported in Table I agree with the values assigned to Er in a biaxial site in YH$_{2.94}$ by Venturini.\textsuperscript{13} No specific assignments were made for the Dy: YH$_3$ spectrum.

Gd$^{3+}$ gives a single isotropic line at $g = 1.996$ in YH$_2$ and $g = 1.96$ in LaH$_{2.0}$ as expected for an S-state ion, although the zero-field splitting expected even in a cubic environment\textsuperscript{12} is absent. Such collapse of a zero-field multiplet into a single line is characteristic of exchange narrowing through coupling via conduction electrons as is found for Gd in gold\textsuperscript{20} and for Gd in d-band intermetallic compounds.\textsuperscript{21} The broadening of the Gd$^{3+}$ resonance line in LaH$_x$ as $x$ increases from 2.0 to 2.6 could reflect either the decrease in conductivity or the decrease in site symmetry, or both, as hydrogen occupies additional octahedral sites. The complex spectra obtained for Gd$^{3+}$ in YH$_3$ show that exchange narrowing by coupling through conduction band electrons is no longer effective as the hydride loses its metallic character.

The absence of EPR signals for Er and Dy in LaH$_{2-3}$ could be due to a number of factors. First of all the experiments were performed at \textasciitilde 10$^\circ$K where as Venturini has shown that cubic lines could be considerably broadened.\textsuperscript{13} Secondly, the concentrations of Er and Dy were considerably higher than in the YH$_{2-3}$ samples which also could cause line broadening.
This work and Venturini's work show that considerable information may be obtained from EPR experiments on hydridic materials and point the way for future experiments.

Acknowledgements

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References


Table I. Summary of EPR Observations at \( \sim 10^\circ\text{K} \).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mol. %</th>
<th>Host</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er(^{3+})</td>
<td>0.6</td>
<td>YH(_2)</td>
<td>Single line, ( g = 6.60 \pm 0.05 ), ( \Delta H = 125 ) gauss</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>YH(_3)</td>
<td>Complex spectrum, principal lines at ( g = 10.9, 5.0, 3.7 )</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>LaH(_{2-3})</td>
<td>No spectra observed</td>
</tr>
<tr>
<td>Dy(^{3+})</td>
<td>1</td>
<td>YH(_2)</td>
<td>Single line, ( g = 6.9 \pm 0.2 ), ( \Delta H = 287 ) gauss</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YH(_3)</td>
<td>Weak lines at ( g = 6.1 \pm 0.5 ) and ( g = 14 \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>LaH(_{2-3})</td>
<td>No spectra observed</td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>2</td>
<td>YH(_2)</td>
<td>Single line, ( g = 2.00 \pm 0.02 ), ( \Delta H = 305 ) gauss</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>YH(_3)</td>
<td>Complex spectrum from ( g = 19 ) to 1.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>LaH(_{2.0})</td>
<td>Single line, ( g = 1.96 \pm 0.04 ), ( \Delta H = 195 ) gauss</td>
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<tr>
<td></td>
<td>5</td>
<td>LaH(_{2.4})</td>
<td>Single line, ( g = 1.96 \pm 0.04 ), ( \Delta H = 300 ) gauss</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>LaH(_{2.6})</td>
<td>Single line, ( g = 2.00 \pm 0.05 ), ( \Delta H = 433 ) gauss</td>
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