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To cite this version:

HAL Id: jpa-00219607
https://hal.archives-ouvertes.fr/jpa-00219607
Submitted on 1 Jan 1980

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MOSSBAUER STUDIES OF HYDROGEN-ABSORBING RARE-EARTH INTERMETALLICS

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ABSTRACT

Mossbauer spectroscopy has been used to study both the physics and phenomenology of hydrogen absorption in rare-earth intermetallics. This paper surveys experiments that have been carried out so far, and discusses the results obtained.

LaNi₅ and similar intermetallic compounds have been of great interest recently because of their ability to absorb reversibly large amounts of hydrogen at convenient temperatures (0-100°C) and pressures (0.1-100 atm) with rapid kinetics. These properties have become the basis of hydrogen pumps, batteries, gas absorption air conditioners, and bulk hydrogen storage facilities. One of the major advantages of LaNi₅ is that the temperature and pressure dependence of its hydrogen desorption curve can be "designed" for a particular application by alloying other elements with the La or Ni.

An effective semi-phenomenological theory has been developed to explain the stability of the ternary hydrides, and, to a great extent, to predict possible new families of useful materials. LaNi₅ and its pseudobinary alloys have been studied well enough to allow prediction of thermodynamic properties which are of importance for most applications listed above.

Studies by photoelectric spectroscopy and neutron diffraction have also been carried out to determine the microscopic mechanism by which hydrogen is incorporated into these materials.

An important aspect of these materials is that the hydrides form as ternaries with a distinct and well-defined hydrogen stoichiometry. This is in contrast to, e.g., Ta, which dissolves hydrogen over a wide range of solid-solution concentrations. Some materials form only one hydride (e.g., LaNi₅ → LaNi₅H₆.7), while others form hydrides with two or more hydride phases. These can be observed by x-ray crystallographic studies, the gas evolution isotherm, or Mössbauer spectroscopy.

Mössbauer spectroscopy has the advantage of being a truly microscopic probe of materials. It is capable of studying these intermetallics over a wide range of temperature, and while they are actually under hydrogen pressure. Since neither La nor Ni are desirable Mössbauer isotopes, the studies carried out to date have all been on LaNi₅ with a small quantity of another rare-earth (RE) substituted for the La, or on other RE-transition metal intermetallics which could be expected to behave similarly.

Five basic phenomena have been studied in experiments to date (see Table I):

1. In polyphase samples, the individual phases can be identified and quantified.
2. The magnetism of the sublattices can be studied via the hf interaction.
3. The isomer shift provides a unique indicator of changes in the electronic structure under hydriding.
4. Oxidation can be readily observed.
5. The Mössbauer spectrum can be used to assay the amount of absorbed hydrogen, and thus to diagnose degradation mechanisms.

In the discussion below, these points are illustrated by selections from the work listed in Table I.

A clear early example of the first point is ref. 12, some results of which are shown in Fig. 1. Using the Gd155 resonance as a probe in LaNi₅, the measurements show that the spectrum of Gd:LaNi₅H₆.7 (the saturated hydride) differs in is. and quadrupole splitting from that of Gd:LaNi₅, and that the spectrum of a partially hydrided sample can be explained as being a sum of spectra of the intermetallic and the saturated hydride. This result is important in showing that even on a microscopic scale the hydride is not continuous solid solution. Similar results were found for LaCo₅, but in that case, more than one hydride is formed. Several subsequent experiments with Eu compounds showed similar results.

For RE intermetallics with Fe, the hf field and moment at the Fe site usually change slightly for the lower hydrides (H/RE = 4), but decrease strongly for the higher hydrides. The iron sublattice in ErFe₂H₄.12 is virtually nonmagnetic, even at 1.7 K (see Fig. 2). In Fe-RE systems in which the iron sublattice provides a large exchange field for the RE ions
TABLE I: MOSSBAUER STUDIES OF HYDROGEN-ABSORBING RARE-EARTH INTERMETALLICS

<table>
<thead>
<tr>
<th>Intermetallic</th>
<th>Isotope</th>
<th>Hydride $x^\approx$</th>
<th>Conclusions</th>
<th>Group, References</th>
</tr>
</thead>
<tbody>
<tr>
<td>YFe$_2$, GdFe$_2$</td>
<td>Fe$^{57}$</td>
<td>$\approx 4$</td>
<td>Greatly reduced Fe-Fe exch. slightly incr. $H_{\text{eff}}$ for YFe$_2$H$_4$. Very broad lines. Isomer shift changes.</td>
<td>Philips 5, 6</td>
</tr>
<tr>
<td>CeFe$_2$, ThFe$_3$</td>
<td>Fe$^{57}$</td>
<td></td>
<td>Local inhomogeneities giving very broad lines no $\alpha$-Fe.</td>
<td></td>
</tr>
<tr>
<td>EuPd, EuNi$_5$, EuRh$_2$, EuMg$_2$</td>
<td>Eu$^{151}$</td>
<td>EuRh$_2$H$_5$</td>
<td>Eu$^{5+}$Eu$^{2+}$ (EuNi$_5$, EuRh$<em>2$) I.S., $H</em>{\text{eff}}$, $T_c$ for hydrides close to EuH$_2$ values. Only saturated and dehydride phases. &quot;Molecular complex&quot; model of hydride formation.</td>
<td>Bell-Philips 7, 8</td>
</tr>
<tr>
<td>DyMn$_2$, DyFe$_2$, DyCo$_2$, DyNi$_2$, Dy</td>
<td>Dy$^{161}$</td>
<td>2, 3.45, $&gt;4$</td>
<td>DyTm$_2$H$_x$ I.S. like that of DyH$_2$, DyH$_3$. Reduced cond. el. density. Greatly reduced TM-Dy exchange. Support of RE-H &quot;complex&quot; model.</td>
<td>9</td>
</tr>
<tr>
<td>EuRh$_2$</td>
<td>Eu$^{151}$</td>
<td>5 − 2</td>
<td>Reversibly absorbed H$_2$ decreases after a few cycles - formation of fixed hydride.</td>
<td>10</td>
</tr>
<tr>
<td>La$<em>{0.9}$Eu$</em>{0.1}$Ni$_5$</td>
<td>Eu$^{151}$</td>
<td>6 − 3</td>
<td>Reversibly absorbed H$_2$ decreases after hundreds of cycles. Formation of a fixed hydride</td>
<td>Bell 11</td>
</tr>
<tr>
<td>La$<em>{0.9}$Gd$</em>{0.1}$Ni$<em>5$, La$</em>{0.9}$Gd$_{0.1}$Co$_5$</td>
<td>Gd$^{155}$</td>
<td>$&lt;6.7$</td>
<td>Spectra show only distinct hydride phases. Reduced s-density at Gd nucleus</td>
<td>Hebrew Univ. 12</td>
</tr>
<tr>
<td>ErFe$_2$</td>
<td>Fe$^{57}$</td>
<td>3.65, 4.12</td>
<td>Greatly reduced $T_c$ and Fe-Er exchange. Negligible Fe moment and $H_{\text{eff}}$ in ErFe$_2$H$_4$.12.</td>
<td>Argonne 13</td>
</tr>
<tr>
<td>DyFe$_2$</td>
<td>Fe$^{57}$</td>
<td>1.92</td>
<td>Reduced Dy-Fe exchange.</td>
<td>14</td>
</tr>
</tbody>
</table>

Fig. 1. Quadrupole-split Gd$^{155}$ spectra in LaNi$_5$ and hydrides. Spectrum of the partially hydrided material is composed of components from the unhydrided material and the saturated hydride (Ref. 12).
Iron sublattice appears nonmagnetic, even at 1.7 K (Ref. 13).

The open points are for the fresh materials, the filled points for the saturated hydrides. For all compounds studied, both IS and H_{int} for the hydrides are close to those of EuH_{2} (Ref. 8).

were carried out on LaNi_{5} doped with small amounts of Eu and Mn. This material has essentially the same absorption properties as LaNi_{5}. Control experiments (Fig. 5 A, B, C) show that the Eu is trivalent in the original material, becomes Eu^{2+} in the hydride, and returns to Eu^{3+} when the hydrogen is removed. It thus serves as an excellent indicator of the amount of hydrogen in the sample.

Measurements carried out with automated cycling apparatus showed that after 1500 absorption-desorption cycles, the material retained only 29% of its original capacity to absorb hydrogen reversibly, measured by the evolved gas volume. The Mössbauer measurements (Fig. 6 D, E) showed that this effect resulted from the formation of a permanent hydride phase, which could not be decomposed at room temperature. The Mössbauer and gas volume measurements were in quantitative agreement on the amount of the permanent hydride phase. Since the peak of Eu^{3+} in Eu_{2}O_{3} is easily resolved from that of Eu^{3+} in LaNi_{5}, the spectrum (Fig. 5 D) showed that very little oxidation had occurred during the cycling. This confirmed that the degradation was the result of an intrinsic mechanism, rather than simply oxidation. Thermodynamic arguments show that the formation of RE hydride and nickel metal is energetically preferred to formation of the ternary hydride. Thus, in principle, this effect should occur. In fact, it has been observed in La_{7}Ni_{3}. However, our observations are the first of this kind in an intermetallic normally considered to be a reversible absorber.
The material above shows that there is a great deal that can be learned via Mössbauer spectroscopy about the physics and phenomenology of hydrogen absorption. Once the materials and hydrogen volume apparatus are at hand, the measurements are relatively easy and provide useful information. Areas which would be particularly appropriate for further work would be (1) Fe$^{57}$ studies of Fe doped LaNi$_5$, (2) calculations of wave functions for the hydrides, for comparison with the results of Mössbauer experiments, and (3) RE Mössbauer measurements to detect oxidation in intermetallics used as hydrogen absorbing electrodes in contact with aqueous electrolytes.

REFERENCES