

Experimental and theoretical study of the behavior of hydrogen in rare earths

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Abstract

In this work, we study the behavior of hydrogen in some rare earths lanthanum (La), cerium (Ce), lutetium (Lu), and in two of its chemical precursors, scandium (Sc) and yttrium (Y).

In the experimental aspect, samples of pure La were hydrided by direct contact with hydrochloric acid. In order to evaluate the influence of acid concentration on the hydriding, two different concentrations (12 and 1.2M) were tested. The hydrogen content was measured by means of a LECO equipment and the hydriding fronts were observed by optical and scanning electronic microscopy.

From the theoretical point of view, we determine some fundamental properties such as: screening charge density, volume of solution of hydrogen, heat of solution and variation of the density of states. Using a program based on the theory of the functional density, we model the material as an “effective jellium” (Phys. Rev. B 22 (1980) 1564).

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1. Introduction

The technological interest for rare earths has been stimulated by different processes which use individual rare earths as metals and as salts. One of these applications is the use of mixed rare earths (*mischmetal*) for petroleum cracking.

Another area of great interest is the interaction of rare earths with hydrogen. From an applied point of view, this interaction has great interest due to the increasing development of AB₅-type alloys (where A and B are rare earths or a rare earths mix) as hydrides for the storage of energy

as hydrogen. The study of these compounds comes from the need of substituting petroleum by any other cleaner and cheaper fuel for internal combustion engines. These technological developments are also associated to rare earths extraction and purification costs [1].

The study of hydrided pure rare earths constitutes the fundamental tool in order to understand the basics of the hydriding process and allows to extrapolate results to alloys. In the present work, experimental details of La hydriding are shown and a theoretical study of different rare earths of the periodic table is developed.

2. Experimental results

The objective of the experimental work was to measure the quantity of hydrogen absorbed by the samples of La (approx. of 3 mm of length) when they are put in contact with

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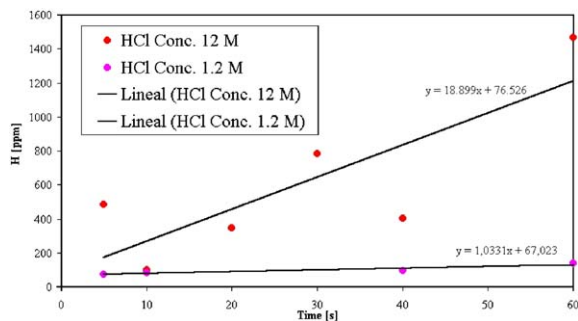


Fig. 1. Hydrogen in La samples, as a function of the contact time.

hydrochloric acid (HCl) and to determine the influence of acid concentration and contact time in the hydriding process. Several samples of La 99.9% were included in acrylic and polished (till 600 paper), to eliminate the oxide surface layer. The hydriding was made by “quick way”, using a hyssop embedded in hydrochloric acid, with two different solutions: a concentrated one (12 M), and a diluted one (1.2 M). After the hyssop contact, the samples were rinsed with water to stop the reaction. This procedure was rehearsed with five contact times between 5 and 60 s. Before doing the hydrogen content measurements, the samples were cleaned with pure acetone.

The reaction that took place was the following one:



where the chlorine goes as a gas.

For the measurement of the hydrogen concentration in the samples of hydrided La, we used a LECO EF-400 RH-404 equipment, operative principle of which is based on the comparison of the thermal conductivity of a current of pure argon (used as blank) and that of another current of argon that has hydrogen released by the melted sample. An electrode furnace gives a power of 1500 W, heating the graphite crucible with the sample till 1200 °C. This value is higher than La melting point (920 °C). As the hydriding is superficial, the hydrogen concentrations (in weight ppm) were corrected by a factor that takes into account the mass relation of the different samples, in order to make them comparable.

In Fig. 1 we observe that the hydriding with diluted solution (1.2 M) is very poor and presents a linear tendency. On the other hand, the curve for the concentrated solution (12 M) presents an increasing hydriding for increasing times and does not follow a linear behavior, but we used a linear regression to adjust values.

In Figs. 2 and 3 of scanning electronic microscopy (SEM) and optical microscopy (OM), we observe the layer of hydride that grows as a surface front that has been formed on the La sample.

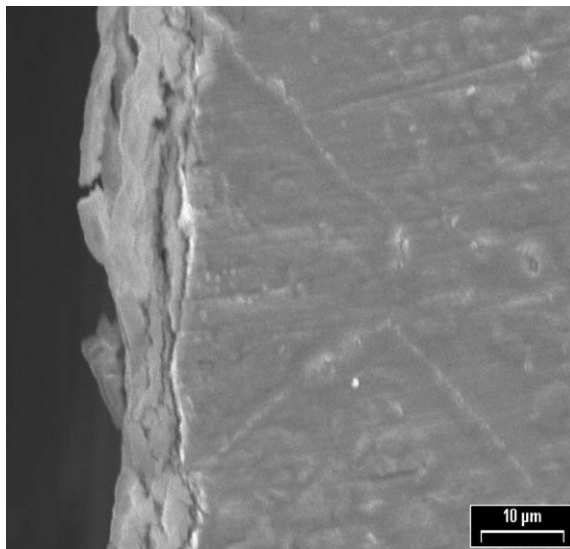


Fig. 2. Hydride front in La obtained by SEM.

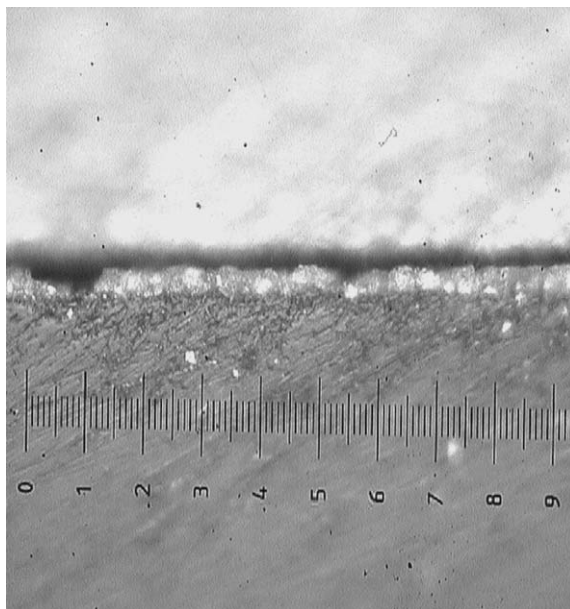


Fig. 3. La hydride layer determined by MO.

3. Results obtained from theoretical modelling

In the theoretical aspect, the objective of this work is to study some important physical properties of the hydrogen–rare earth systems such as the volume of solution of hydrogen, the difference in enthalpy and the variation of the density of states (DOS). The rare earths that we consid-

Table 1
Vh, for different values of the magnetic moment σ

Sample	Vh _{jell} (Å ³)	Vh _{exp} (Å ³)	Vh _{tb} (Å ³) [6]
La	4.23	4.25[1]	3.96
Sc	3.14	2.36[1]–1.1[8]	1.17
Y	1.858	3[10]–1.1[8]	1.07
Ce ($\sigma = 0$)	2.224	—	4.46
Ce ($\sigma = 0.3$)	0.267	—	—
Ce ($\sigma = 0.5$)	20.64	—	—
Ce ($\sigma = 0.6$)	32.69	—	—
Lu ($\sigma = 0.4$)	7.11	—	1.35

ered for the calculation are: La, Ce and Lu, and two of its precursors: Sc and Y.

In order to make the corresponding calculations, we used a program based on the formalism of the functional density [2,3] and on the effective jellium model [4] for rare earth. An important quantity to determine, when an impurity is introduced in the electronic gas, is the screening charge density Δn induced by this impurity. From this quantity, we can obtain the volume of solution and the heat of formation.

3.1. Volume of solution of hydrogen Vh

We obtain the value of the volume of solution of hydrogen in the selected rare earth as a function of the variation of the screening charge density Δn and of the characteristic parameters of the effective jellium model [4]. The corresponding values are shown in Table 1 and compared with reliable experimental data and with those obtained with the semi-empirical tight binding model (tb). For Ce we also performed the calculation for different values of the magnetic moment of spin (σ), as given by the behavior of the f itinerant electron [5,6].

3.2. Heat of solution ΔH

If the jellium model were exact, the value of the variation of the enthalpy would be equal to the variation of the total energy of the system: $\Delta H \approx \Delta E$. Here the total energy E is defined as the sum of the kinetic energy of the non-interactive system of the electron gas, the exchange and correlation energy and the classic electrostatic energy. As the jellium model is not exact, ΔH must be calculated from the following equation:

$$\Delta H = \alpha \Delta E + \beta, \quad (1)$$

where α and β are parameters of the fitting model: $\alpha = 28.5 \pm 9$ kJ/mol H eV and $\beta = 358.8 \pm 140$ kJ/mol H .

We obtain the values ΔE and ΔH for the analyzed elements as a function of the parameterization of Eq. (1), and compare them with values found in the bibliography (Table 2).

Table 2
Total energy and heat of solution of hydrogen

Sample	ΔE_{jell} (kJ/mol)	ΔH_{exp} (kJ/mol) [7]
La	−62.73	−96.49
Sc	−54.08	−86.72
Y	−59.04	−95
Lu	−66.15	—
Ce	−43.80	—

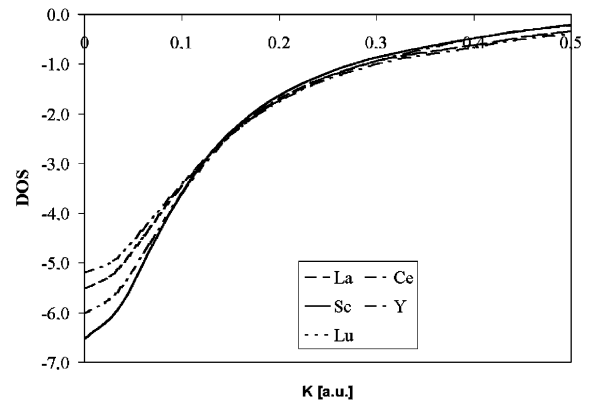


Fig. 4. Induced density of states as function of the wave vector k .

3.3. Variation of induced density of states DOS

Another important quantity to determine when an impurity is introduced in the material is the induced DOS, since this quantity is related to the electronic structure of the system. The method used provides the behavior of the density of states as function of the energy of the system (or equivalently of the wave vector k) and of the angular total moment l of the system [8]. We obtained a parameterization (of null spin) of the general behavior of this induced density of states, shown in Fig. 4.

3.4. Behavior of cerium

The itinerant f electron gives Ce different spin values, resulting in different behaviors [4]. We show in Figs. 5 and 6 the induced DOS for different values of the magnetic moment of spin for which magnetic transitions occur. We find that 0.5 is the critical value of the magnetic moment for these transformations.

4. Conclusions

From the experimental point of view, the measured values of hydrogen concentration in La show that the treatment with concentrated HCl is a promising tool for obtaining

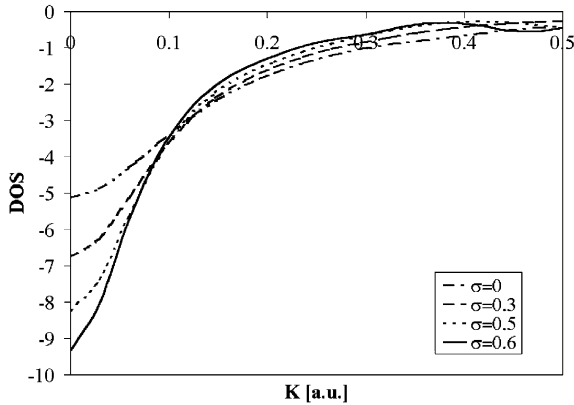


Fig. 5. Variation of DOS as function of the wave vector k for different values of the magnetic moment of Ce.

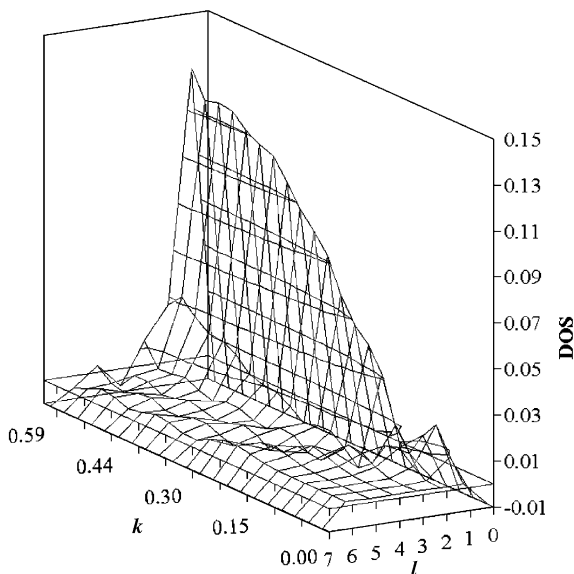


Fig. 6. Variation of DOS of H in Ce, as function of quantum number l for different values of k . The curves of other values of the magnetic moments are qualitatively similar.

samples of hydrided lanthanum. With an additional thermal treatment, we could obtain homogenized distributions of the hydride phase. No important effect was detected with HCl diluted solution and the final values of hydrogen concentration are close to the sample background.

With respect to the theoretical calculations, we can conclude the following;

Vh: As we see in Table 1 the volumes of solution of La, Y and Sc obtained with the effective jellium model agree with the experimental data and with those values obtained with the tight binding model. For Lu we obtained a value of Vh, corresponding to a magnetic moment of 0.4, which again is not comparable with those of other references. However,

the value of the magnetic moment was not known in those previous studies. With respect to cerium we present several values of the volume of solution of hydrogen corresponding to different values of the magnetic moment, as produced by its f itinerant electron. A detailed discussion of this behavior escapes the original purpose of this work.

ΔH : With respect to the calculated heat of solution we see that the effective jellium model is a very good approximation that allows, with an adequate parameterization, to obtain this quantity in a simple and reliable way.

DOS: As we see in Fig. 3, the induced density of states due to the H presents a similar structure for all the considered elements. This behavior is also similar for Ce (Fig. 4) with its different values of magnetic moment. This is due to the fact that the structure of the induced density of states is dominated by the s part ($l = 0$) of this density of states, but its magnitude varies with the surrounding.

To conclude, we propose to still use the jellium model to study some properties derived of the screening density charge of rare earth elements. However, we need to take into account that the values of r_s parameter must be taken from the given experimental values of the bulk modulus B .

This method is simple and general and gives satisfactory results for the chosen rare earths, and can be advantageously used as long as sufficiently accurate first principle calculations are not available.

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