

## INFLUENCE OF SUBSTITUTION AND STOICHIOMETRY ON THE STRUCTURAL PROPERTIES OF $RM_5$ -TYPE HYDRIDE FORMING COMPOUNDS

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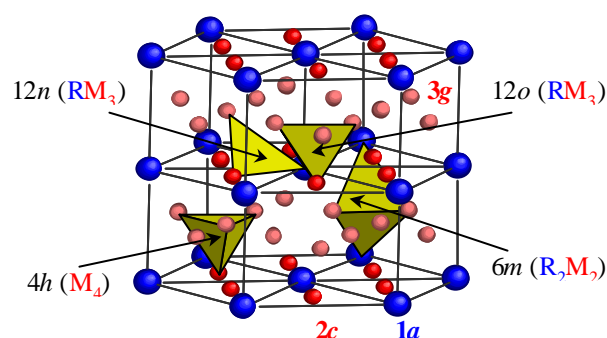
### Introduction

Neutron powder diffraction is a very useful tool for the characterisation of intermetallic compounds and metallic hydrides. For the intermetallic compounds, substitution on the metal sublattice is commonly used to tune their thermodynamic properties. Substituting elements are generally neighbours in the periodic table and show poor contrast using classical X-ray powder diffraction. This problem can be overcome by neutron diffraction since neighbouring elements can have quite different Fermi lengths allowing determination of the substitution rates on the different available crystallographic sites within the structure. Concerning the hydrides (or deuterides since deuterium is usually preferred to hydrogen according to its lower background contribution), neutron diffraction is crucial for the determination of the structural properties of the hydrogenated phase: symmetry, nature of occupied insertion sites and occupation factor. Moreover, due to the large neutron penetration depth, structural studies can be performed in closed cell under hydrogen pressure up to 100 bar allowing accurate control of the hydrogen composition

### Scientific background

Most of the intermetallic alloys of general formula  $RM_n$  (R : rare earth or transition metal; M : transition metal ;  $n=5, 2$  or  $1$ ) are able to store large amounts of hydrogen to form metallic hydrides. The absorption/desorption reaction is reversible in a large domain of temperature and pressure. Therefore those compounds have been developed for energy storage applications. Among them, electrochemical storage of hydrogen leads to large capacity negative electrodes in  $NiOOH/Ni(OH)_2|KOH|RM_n/RM_nH_x$  type batteries [1]. Among the hydride forming compounds,  $LaNi_5$  is able to store more than 7H per formula unit at room temperature.

The reaction occurs following the reversible equation:  $LaNi_5 + x/2 H_2 \rightleftharpoons LaNi_5H_x$ . This reaction implies a transition between the intermetallic compound ( $\alpha$  phase) and its hydride ( $\beta$  phase) at a constant hydrogen pressure. This plateau pressure is related to the enthalpy of formation of the hydride by the Van't Hoff's law following the relation  $\ln(P_{eq}) = \Delta H/RT - \Delta S/R$ . However, this equilibrium pressure, above the atmospheric one for  $LaNi_5$ , is not suitable for electrochemical applications. It can be modified by convenient substitutions on R and/or M sublattice. Keeping the hexagonal  $CaCu_5$ -type structure (figure 1) of the parent intermetallic compound, substitutions involve cell volume variations and it has been shown that a linear correlation exists between the cell volume deviations and the plateau pressure logarithm [2].



**Figure 1** -  $CaCu_5$ -type structure for intermetallic compounds  $RM_5$  : Space group  $P6/mmm$ , R (1a), M (2c), M' (3g). Nature and symmetry of the H/D occupied sites are shown as tetrahedra. For sake of clarity, the cell has been doubled along the c axis.

This behaviour is attributed to the correlation existing between the geometrical size and the energy well of the hydrogen occupied sites. It can be directly related to the enthalpy of formation of the hydride. By substitution on the Ni sites by elements such as Mn, Al or Co, it is then possible to decrease the plateau pressure and to improve the cycle life of battery materials without significant loss of the storage properties [3]. The capacity decrease on cycling is commonly attributed to the decomposition of the alloy and to the formation of lanthanum hydroxide [4]. It was shown that the corrosion process was directly related to the cycling effect and explained by the cell volume expansion observed during hydrogen absorption. By adequate substitution, reduced volume expansion is obtained

## Structures and Phase Transitions

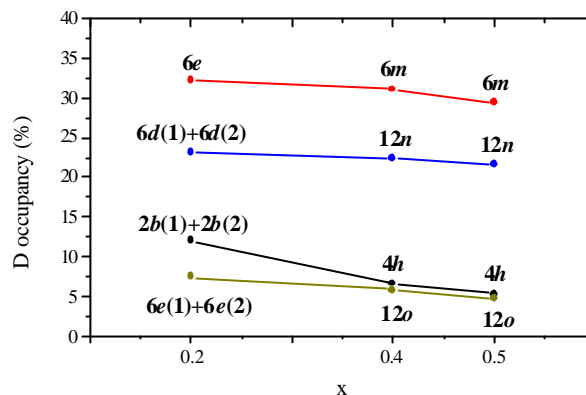
involving less internal stresses, less decrepitation and thus less new surfaces in contact with the highly oxidizing electrolyte.

Beside the substitution effects, reduced cell volume variations can also be achieved by preparing superstoichiometric compounds. These  $RM_{5+x}$  compounds, which contain an excess of chosen M-type elements (Ni, Mn, Cu or Sn), are obtained by substituting part of the R atoms in the crystal by dumb-bells of M atoms [5]. Such effect is of interest since electrode materials made from overstoichiometric alloys present in addition better cycle life than stoichiometric ones [6]. Again, this is related to the discrete lattice expansion between the  $\alpha$  and the  $\beta$  phases. This has been proved on overstoichiometric compounds  $La(Ni_{1-y}Cu_y)_{5+x}$  and  $La(Ni_{1-y}Mn_y)_{5+x}$  [7-9] for which excellent cycle life was connected to the low decrepitation and the small discrete lattice expansion upon cycling.

### Results

Different substitutions of nickel by other elements (Co, Al, Mn) have been studied so far and substitution rates between the two available Ni sites have been achieved taking advantage of the better contrast provided by means of neutron diffraction analysis for these elements. In the case of tin, substituted compounds possess exceptional long term stability as regard to hydrogen cycling in gas storage applications. The crystal structures of three  $LaNi_{5-x}Sn_x$  compounds ( $x=0.2, 0.4$  and  $0.5$ ) and their deuterides have been investigated [10]. For each composition of the intermetallic compounds, it has been shown by neutron diffraction that tin substitutes only for nickel and is located on site  $3g$ . Concerning the deuterides, for  $x=0.5$  and  $x=0.4$ , deuterium occupies four interstitial sites of space group  $P6/mmm$ :  $4h$  ( $1/3, 2/3, z=0.38$ ),  $6m$  ( $x=0.14, 2x, 1/2$ ),  $12n$  ( $x=0.47, 0, z=0.11$ ),  $12o$  ( $x=0.21, 2x, z=0.33$ ). On the contrary, for  $LaNi_{4.8}Sn_{0.2}D_{6.1}$ , a decrease of symmetry from  $P6/mmm$  to  $P6mm$  (keeping the same cell) is observed. It is due to ordering of deuterium atoms: site  $4h$  splits into two sites  $2b$ ,  $12n$  into two  $6d$ ,  $12o$  into two  $6e$ ,  $6m$  is conserved in  $6e$ . This behaviour is summarised on figure 2 that shows the evolution of the site occupancy as a function of tin content  $x$ . The deuterium ordering is attributed to the higher capacity observed for this compound (6.1 D per

formula unit) compared to 5.8 and 5.2 for  $x=0.4$  and  $0.5$  respectively. Indeed, due to electrostatic interaction between protons, high concentration leads to exclusion rules between adjacent sites and involves hydrogen ordering [11,12].



**Figure 2** - Deuterium occupancy factors as a function of tin composition in  $LaNi_{5-x}Sn_x$  deuterides. For low tin concentration, a symmetry lowering from  $P6/mmm$  into  $P6mm$  and a splitting of the deuterium sites is observed.

In battery applications, for cost reasons, lanthanum can be replaced by mismetal (Mm), a mixture of rare earths essentially composed of La, Ce, Nd and Pr. However, cerium can play a significant role in the behaviour of these materials. Substitution of lanthanum by cerium has therefore been investigated [13]. The thermodynamic properties of hydrogen absorption by  $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$  and  $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ , two potential materials for nickel-metal hydride batteries, as well as the structural properties of their hydrides, have been studied and compared.

The cerium compound has a smaller cell volume and consequently higher equilibrium pressure. The  $\alpha$  phase region is more extended in this latter compound and the plateau, keeping the same width, is shifted towards higher hydrogen compositions. This is attributed to a better occupancy of hydrogen sites  $6m$  in both  $\alpha$  and  $\beta$  phases as it has been determined by neutron diffraction analysis (figure 3). It can be related to an increased site size in the intermetallic compound. Anomalous behaviour of both cell volume expansion and  $6m$  site filling was also observed (figure 3). Such behaviour has been interpreted by a valence change of cerium upon hydrogenation, later confirmed by X-ray absorption near edge spectroscopy [14].

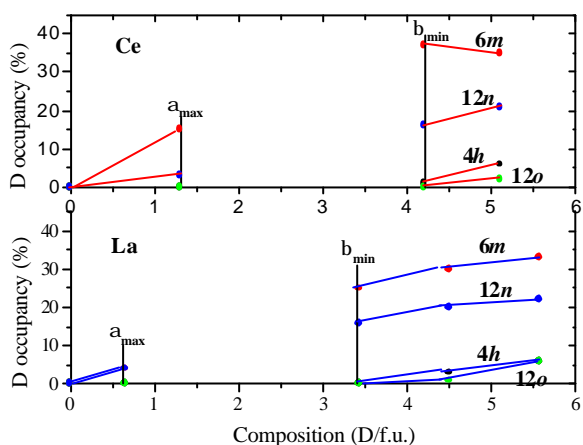


Figure 3 - Occupancies of the deuterium sites as a function of the deuteride composition for  $\text{LaNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.75}$  and  $\text{CeNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.75}$ .

Finally, the influence of superstoichiometry on the structural properties has been considered. Several hydrides belonging to the  $\text{LaNi}_{5+x}\text{D}_y$  system have been studied. For  $x=0.2$  and  $y=6$ , superstructure lines involving a doubling of the  $c$  axis are observed. These results have to be compared to the crystal structure of stoichiometric  $\text{LaNi}_5\text{D}_7$  [15] for which the same ordering effect is observed. For  $x=0.4$  and  $y=5.7$  D per formula unit, this superstructure is no longer observed and a possible decrease of the symmetry to  $P6mm$  space group is considered. This structural change is probably due to the lower capacity (5.7 D) observed for this overstoichiometric compounds but the influence of dumb-bells has also to be taken into account. According to these results, overstoichiometry can provide similar effects on both structural and thermodynamic properties than metallic substitution. Therefore it can be an alternative to substitution by costly elements like cobalt for instance.

Better knowledge of the structural properties of metallic hydrides as a function of substitution and stoichiometry remains very important for the optimisation of these energy storage materials. Substituents localisation, nature and rate of the occupied hydrogen sites can be achieved by neutron diffraction analysis. This technique allows data collection in closed cell under controlled deuterium gas pressure leading to accurate and unambiguous structural determination at various D concentration.

[1] Percheron-Guégan, A., Achard, J.-C., Sarradin, J. and Bronoël, G. *Electrode Material based*

*on Lanthanum and Nickel, Electrochemical uses of such materials.* US patent 688537 (1978).

- [2] Achard, J.-C., Percheron-Guégan, A., Diaz, H., Briaucourt, F. and Demany, F. 2nd Int. Congr. on Hydrogen in Metals. Paris (1977) 1E12.
- [3] Percheron-Guégan, A., Latroche, M., Achard, J. C., Chabre, Y. and Bouet, J. Hydrogen and Metal Hydride Batteries, Pennington, NJ, USA. The Electrochemical Society Proceedings Series (1994) 196-219.
- [4] Willems, J. J. G., *Suppl. Philips J. Res.*, **39** (1984) 1.
- [5] Latroche, M., Joubert, J.-M., Percheron-Guégan, A. N. and Notten, P. H. L., *J. Solid State Chem.*, **146** (1999) 313-321.
- [6] Latroche, M., Chabre, Y., Percheron-Guégan, A., Isnard, O. and Knosp, B., *J. Alloys Compd.*, **in press** (2001).
- [7] Notten, P. H. L., Daams, J. L. C. and Einerhand, R. E. F., *J. Alloys Compd.*, **210** (1994) 233.
- [8] Notten, P. H. L., Einerhand, R. E. F. and Daams, J. L. C., *J. Alloys Compd.*, **210** (1994) 221.
- [9] Notten, P. H. L., Latroche, M. and Percheron-Guégan, A., *J. Electrochem. Soc.*, **146** (1999) 3181-3189.
- [10] Joubert, J.-M., Latroche, M., Cerný, R., Bowman, R. C. J., Percheron-Guégan, A. and Yvon, K., *J. Alloys Compd.*, **293-295** (1999) 124-129.
- [11] Percheron-Guégan, A., Lartigue, C. and Achard, J.-C., *J. Less-Common Met.*, **109** (1985) 287.
- [12] Latroche, M., Rodriguez-Carvajal, J., Percheron-Guégan, A. and Bourée-Vigneron, F., *J. Alloys Compd.*, **218**, 1 (1995) 64-72.
- [13] Joubert, J.-M., Latroche, M., Percheron-Guégan, A. and Bourée-Vigneron, F., *J. Alloys Compd.*, **275-277** (1998) 118-122.
- [14] Paul-Boncour, V., Joubert, J.-M., Latroche, M. and Percheron-Guégan, A., *J. Alloys Compd.*, **in press** (2001).
- [15] Lartigue, C., Le Bail, A. and Percheron-Guégan, A., *J. Less-Common Met.*, **129** (1987) 65.