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# Investigation of structural and hydrogen absorption properties in the $LaNi_{5-x}Pt_x$–$H_2$ system

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**Abstract**

The substitution of nickel by platinum in the binary $LaNi_5$ compound ($CaCu_5$ structure type, $a = 5.019(1)$ Å, $c = 3.981(1)$ Å, space group $P6/mmm$) and its effect on the hydrogenation properties was studied. The phase $LaNi_{5-x}Pt_x$ has a homogeneity domain ranging from $x = 0$ to 5. For $x < 3$, platinum substitutes almost exclusively on site $3g$ and also replaces nickel on site $2c$ for $x > 3$. Contrary to what is observed in other systems, the hydrogen absorption plateau pressure was found to increase as a function of the cell volume. Powder neutron diffraction experiments were conducted for two deuterated compounds with $x = 0.25$ and 0.75. Deuterium partial ordering occurs in the case of $x = 0.25$ leading to a symmetry decrease to the space group $P6mm$ ($LaNi_{4.75}Pt_{0.25}D_{5.23}$, $a = 4.225(1)$ Å, $c = 5.357(1)$ Å, $Z = 1$, $R_{Bragg} = 3.3\%$). For $x = 0.75$, an orthorhombic superstructure based on the $CaCu_5$-type lattice was found ($LaNi_{4.25}Pt_{0.75}D_{2.61}$, $a_{orth} = \sqrt{3}a_{hex} = 9.089(1)$ Å, $b_{orth} = b_{hex} = 5.272(1)$ Å, $c_{orth} = 2c_{hex} = 8.145(1)$ Å, $Z = 4$, SG $Ibam$, $R_{Bragg} = 6.1\%$).


*Keywords:* $LaNi_5$; Pt; Hydrogen; Hydrogenation properties; Hydrides; Thermodynamic properties; Neutron diffraction; Rietveld refinement

## 1. Introduction

$LaNi_5$ ($CaCu_5$-type structure, space group $P6/mmm$, La in $1a$ (0,0,0), Ni in $2c$ (1/3, 2/3, 0) and $3g$ (1/2, 0, 1/2)) is known to absorb reversibly large amounts of hydrogen (i.e., ~1 hydrogen atom per metal atom) near room temperature and room pressure. In the frame of the development of hydrogen storage compounds, the effects of substitutions in the binary compound on the hydrogenation properties are of primary importance and have been studied for long. In $LaNi_{5-x}M_x$, whereas Al or Mn substitute Ni in relatively small amounts ($x_{max} = 1.25$ or 2.1), Co or Cu, closer in size to Ni, can substitute up to $x = 5$ ($LaCo_5$, $LaCu_5$). As $LaPt_5$ crystallizes with the $CaCu_5$-type structure [1], $LaNi_{5-x}Pt_x$ system offers the uncommon possibility to study the total replacement of Ni by an atom which presents a significant difference in atomic radius ($R_{Ni} = 1.24$ Å, $R_{Pt} = 1.39$ Å). In addition, the strong X-ray contrast between Ni and Pt allows to refine the distribution of Pt on the two available Ni sites and to obtain accurate data on a possible preferential occupancy. Moreover, reported anomaly of the hydrogen absorption pressure of $LaPt_5$ [2] needs clarification by the study of intermediate compositions. Finally, neutron diffraction on deuterated compounds allows comparing the nature and the occupancies of the deuterium interstitial sites to what is observed in other systems.

## 2. Experimental

The intermetallic compounds were synthesized either by induction melting ($x = 0$ to 1) or by arc melting ($x = 2$ to 5) of the pure elements (La, Santoku America Inc., 99.9%; Ni, Materials Research, 99.95%; Pt, Engelhard CLAL, 99.9%). Five meltings were done between which the alloys were inverted. Subsequent annealing treatment was performed under vacuum at 1100°C for different times ranging, depending on the compositions, from 3 h to 4 days. The samples were characterized by optical metallography and electron probe microanalysis (EPMA—Camebax SX100). The powder X-ray diffraction patterns (Bragg–Brentano

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Table 1
Results of the metallurgical and structural characterization of the intermetallic compounds

| Nominal composition | Analyzed composition | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | Pt 2$c$ (atom) | Pt 3$g$ (atom) |
|---|---|---|---|---|---|---|
| $LaNi_5$ | $La_{1.01(1)}Ni_{4.99(1)}$ | 5.019 | 3.981 | 86.84 | 0 | 0 |
| $LaNi_{4.25}Pt_{0.25}$ | $La_{1.01(1)}Ni_{4.73(7)}Pt_{0.26(7)}$ | 5.039 | 3.996 | 87.89 | −0.01 | 0.26 |
| $LaNi_{4.50}Pt_{0.50}$ | $La_{1.01(1)}Ni_{4.49(4)}Pt_{0.49(4)}$ | 5.064 | 4.010 | 89.05 | −0.01 | 0.51 |
| $LaNi_{4.25}Pt_{0.75}$ | $La_{1.00(1)}Ni_{4.22(3)}Pt_{0.78(3)}$ | 5.084 | 4.025 | 90.09 | 0.00 | 0.75 |
| $LaNi_4Pt$ | $La_{1.00(1)}Ni_{3.98(4)}Pt_{1.02(4)}$ | 5.113 | 4.039 | 91.44 | 0.01 | 0.99 |
| $LaNi_3Pt_2$ | $La_{1.01(1)}Ni_{2.97(1)}Pt_{2.02(1)}$ | 5.220 | 4.068 | 96.01 | 0.04 | 1.96 |
| $LaNi_2Pt_3$ | $La_{1.00(1)}Ni_{1.99(1)}Pt_{3.01(1)}$ | 5.332 | 4.098 | 100.92 | 0.14 | 2.86 |
| $LaNiPt_4$ | $La_{1.00(1)}Ni_{0.98(1)}Pt_{4.02(1)}$ | 5.344 | 4.283 | 105.93 | 1.33 | 2.67 |
| $LaPt_5$ | $La_{1.00(1)}Pt_{5.00(1)}$ | 5.392 | 4.380 | 110.28 | 2 | 3 |

The analyzed composition by EPMA, the lattice parameters and Pt occupancy on the two sites 2$c$ and 3$g$ are given. Average standard uncertainties are 0.001 Å on the lattice parameters, 0.05 atom on the occupancy parameters. The total Pt concentration has been constrained to match the nominal composition, resulting in a single refined occupancy parameter.

geometry, $\theta-2\theta$ scan, step scan 0.02° (2$\theta$), scintillator detector, backscattered graphite monochromator, room temperature, Cu $K\alpha$) were analyzed, including the determination of the platinum occupancies on sites 2$c$ and 3$g$, using the Rietveld method (program Fullprof [3]). Constraints were made on the total amount of platinum in order to match the nominal (close to analyzed) stoichiometry. The hydrogenation measurements including hydrogen capacity measurements and determination of the pressure-composition curves at 25°C were done using a conventional Sievert's-type apparatus operating up to 100 bar. The high-pressure measurements (>25 bar) were corrected using an appropriate model for the hydrogen non-ideality [4]. Deuterium was used instead of hydrogen for the powder neutron diffraction measurements. In the absence of any model specific for high-pressure deuterium, the same model as for hydrogen was used. Large quantity (~8 g) sample batches were deuterium loaded on the same device as for the pressure–composition measurements. A silica sample holder was used for $LaNi_{4.75}Pt_{0.25}D_{5.23}$ sample under 13 bar pressure, while an especially designed stainless-steel container was used for $LaNi_{4.25}Pt_{0.75}D_{2.61}$, able to withstand 100 bar deuterium pressure. After absorption, the sample holders were isolated, removed from the loading device and brought to the neutron reactor. The diffraction patterns were measured on 3T2 instrument at the Laboratoire Léon Brillouin in CE-Saclay, France (Debye–Scherrer geometry, step scan 0.05° (2$\theta$), $^3$He multi-detector (20 cells), room temperature, $\lambda = 1.225$ Å) and refined using the Rietveld method. For the first sample, the strong contribution of the silica tube to the background was taken into account by interpolating the background between the diffraction peaks. For the second sample, the austenitic stainless-steel container was taken into account in the refinement without intensity constraint because of a strong texture that is difficult to model.

## 3. Results

All the compounds have been found to be single phase by optical metallography, EPMA and X-ray diffraction. Only in $LaNi_{4.5}Pt_{0.5}$, isolated precipitates were evidenced, that were too small to be identified by EPMA and in too small quantity to give additional lines on the X-ray diffraction pattern. All the results concerning the characterization of the intermetallic compounds are reported in Table 1, including the lattice parameters and the refined distribution of the platinum atoms on the two available sites 2$c$ and 3$g$. The lattice parameters have been plotted in Fig. 1. We observe a large and regular increase of the cell volume with $x$ in agreement with the increase of the atomic radius when replacing Ni ($R_{Ni} = 1.24$ Å) by Pt ($R_{Pt} = 1.39$ Å). However, the plots of $a$, $c$ and $c/a$ ratio indicate that the substitution does not strictly obey to a Vegard's law. The Pt occupancies in sites 2$c$ and 3$g$ are reported in Fig. 2. Two regions can be observed. For $x<3$, Pt tends to substitute almost exclusively on site 3$g$ up to the nearly complete saturation of this site. For $x>3$, site 2$c$ is progressively occupied.

The measured pressure–composition curves at 25°C are reported in Fig. 3 for $0 \leqslant x \leqslant 1$. We note a strong decrease of the capacity and a strong increase of the plateau pressure as a function of the platinum content.

The compound $LaNi_{4.75}Pt_{0.25}$ was studied after hydrogen cycling (15 absorption and desorption cycles) in order to evaluate the hydrogen-induced line broadening in comparison with data previously obtained on several $LaNi_5$ substituted derivatives with synchrotron radiation [5,6]. In the present work, the compound was studied by conventional X-ray diffraction but with a diffractometer setup leading to the best instrumental resolution achievable. The line broadening was corrected with an external $LaB_6$ standard, and as the sample broadening is quite significant, the results are directly comparable with those obtained with

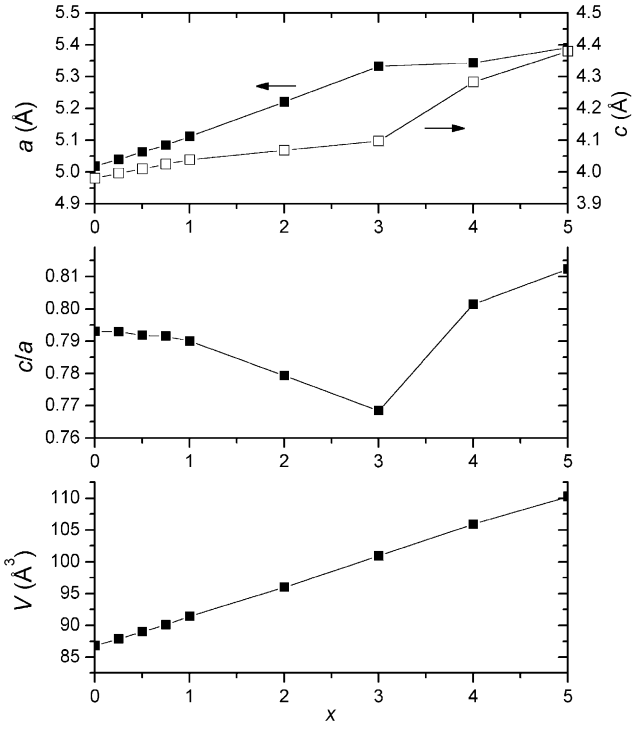


Fig. 1. Lattice parameters, $c/a$ ratio and cell volume as a function of $x$ for $LaNi_{5-x}Pt_x$ compounds.

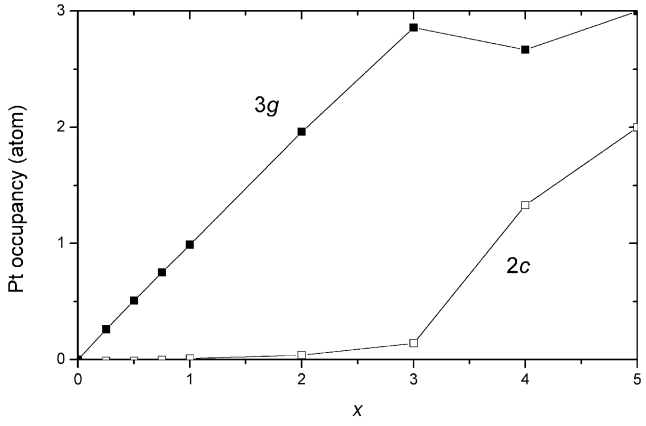


Fig. 2. Platinum occupancies on the two available transition metal sites $2c$ and $3g$ as a function of $x$ for $LaNi_{5-x}Pt_x$ compounds.

synchrotron data. The analysis procedure is detailed in Ref. [5] . Two parameters are refined with the Rietveld program ($S_{AA}$ and $S_{CC}$) to model the strains along $a$ and $c$ axes, respectively. The results give $S_{AA} = 0.55.10^{-3}$ Å$^2$ and $S_{CC} = 0.18.10^{-3}$ Å$^2$ showing strong and mostly anisotropic broadening comparable to what is observed, among the other substituted compounds, for example, in $LaNi_4Fe$. This result is rather surprising if we consider the atomic size of platinum because we have previously observed the trend for the substitution by large atoms (e.g., Sn, Al) to contribute to the suppression of any line broadening in cycled compounds.

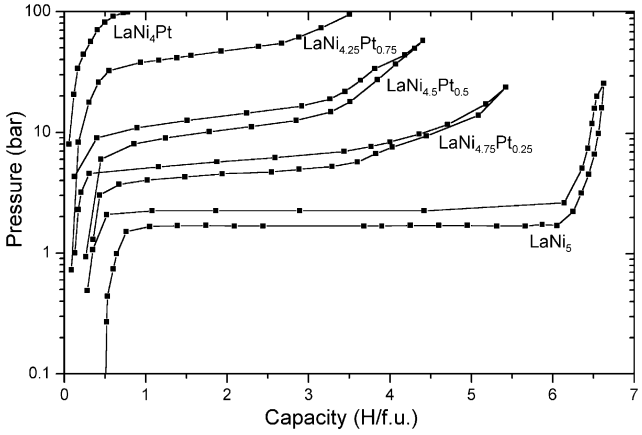


Fig. 3. Hydrogen absorption and desorption (for $x = 0$, 0.25 and 0.5) pressure–composition curves at 25°C for $LaNi_{5-x}Pt_x$ compounds (capacity given in hydrogen atoms inserted per formula unit (f.u.)).

The two samples for neutron diffraction were loaded at the compositions $LaNi_{4.75}Pt_{0.25}D_{5.23}$ and $LaNi_{4.25}Pt_{0.75}D_{2.61}$ under 13.0 and 97.6 bar, respectively. The capacity measured for the second compound differs significantly from the one expected from hydrogen pressure–composition curve and is attributed to a strong isotopic effect of deuterium.

As Ni ($b = 10.3$ fm) and Pt ($b = 9.60$ fm) are nearly indistinguishable with neutron diffraction, the occupancies refined from X-ray diffraction on the intermetallic compounds were kept fixed. The model used in a first step for the refinement has been previously described [7]. It keeps the symmetry of the intermetallic compound (space group $P6/mmm$) and includes the presence of four deuterium interstitial tetrahedral sites ($D_1$ ($4h$), $D_2$ ($6m$), $D_3$ ($12n$), $D_4$ ($12o$)), the occupancy of which can be refined. In the case of $LaNi_{4.75}Pt_{0.25}D_{5.23}$, this model failed to represent the actual composition of the sample (refined D content: 4.5). As was observed on $LaNi_{4.8}Sn_{0.2}D_{6.1}$ [8], the refinement is improved by considering a symmetry lowering to $P6mm$ due to deuterium partial ordering as regards the $P6/mmm$ model. This symmetry change yields the splitting of three among the four interstitial sites ($D_1$, $D_3$, $D_4$). As for tin compound, the atomic positions were refined but kept constrained by the pseudo-mirror symmetry and only distinct occupancy factors were refined for the deuterium split sites. With this model, the agreement factors are significantly improved ($R_{Bragg} = 3.3\%$ instead of 5.9%) and the refined deuterium composition (5.3) matches the nominal one. The anisotropic line broadening already discussed was taken into account in the refinement. Final results are reported in Table 2, Rietveld plot is presented in Fig. 4.

For $LaNi_{4.25}Pt_{0.75}D_{2.61}$, the refinement was first conducted with the $P6/mmm$ model. Low-intensity supplementary lines were found—at the following $d$

Table 2
Results of the powder neutron diffraction refinement of $LaNi_{4.75}Pt_{0.25}D_{5.23}$

| | |
|---|---|
| Nominal composition | $LaNi_{4.75}Pt_{0.25}D_{5.23}$ |
| Space group | *P6mm* |
| *a* (Å) ($\Delta a/a$ (%)) | 5.358 (1) (+6.3%) |
| *c* (Å) ($\Delta c/c$ (%)) | 4.225 (1) (+5.7%) |
| *V* (Å$^3$) ($\Delta V/V$ (%)) | 105.04 (3) (+19.5%) |

| Atom | Site | *x* | *y* | *z* | B (Å$^2$) | Occupancy (atom/cell) |
|---|---|---|---|---|---|---|
| La | 1*a* | 0 | 0 | 0.0 | 1.60(5) | 1 |
| Ni | 2*b* | 1/3 | 2/3 | 0.0 | 2.05(4) | 2 |
| Ni | 3*c* | 1/2 | 0 | 0.5 | 1.45(2) | 2.75 |
| Pt | | | | | | 0.25 |
| $D_{1,1}$ | 2*b* | 1/3 | 2/3 | 0.366(3) | 2.06(8) | −0.02(2) |
| $D_{1,2}$ | 2*b* | 1/3 | 2/3 | $-zD_{1,1}$ | 2.06(8) | 0.43(3) |
| $D_2$ | 6*e* | 0.145(2) | 2*x* | 0.5 | 2.06(8) | 1.31(3) |
| $D_{3,1}$ | 6*d* | 0.465(1) | 0 | 0.101(1) | 2.06(8) | 2.52(4) |
| $D_{3,2}$ | 6*d* | 0.465(1) | 0 | $-zD_{3,1}$ | 2.06(8) | 0.05(3) |
| $D_{4,1}$ | 6*e* | 0.173(3) | 2*x* | 0.366(3) | 2.06(8) | 0 |
| $D_{4,2}$ | 6*e* | 0.173(3) | 2*x* | $-zD_{4,2}$ | 2.06(8) | 1.02(3) |
| D total (atom/cell) | 5.33(18) | | | | | |
| $\chi^2$ | 2.8 | | | | | |
| $R_{Bragg}$ (%) | 3.3 | | | | | |

Deuterium occupancy for site $D_{4,1}$ is refined negatively and is fixed to zero.

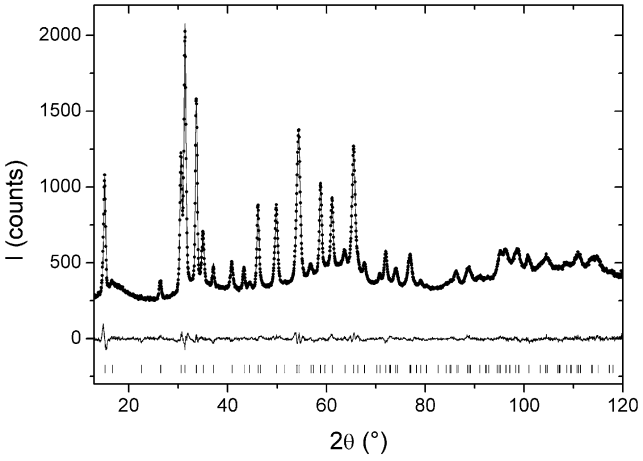


Fig. 4. Neutron diffraction Rietveld refinement pattern of $LaNi_{4.25}Pt_{0.25}D_{5.23}$ under 13.0 bar $D_2$. The observed pattern (dots), the calculated curve (line), the difference curve (line below) and the reflection positions (vertical bars) are plotted. The strong background contribution is due to the silica sample holder.

values: 2.422, 1.475, 1.287, 1.197, and 1.156 Å—that could be indexed properly by using a superstructure based on the $CaCu_5$ lattice ($a_{orth} = \sqrt{3}a_{hex}$, $b_{orth} = b_{hex}$, $c_{orth} = 2c_{hex}$). Among the different possible subgroups of *P6/mmm* in this cell, *Ibam* space group was chosen because the corresponding extinctions are found to occur and it yields the best refinement with fewer parameters among the space groups tested (*Ibmm*, *Imam*, *Immm*, *Im2m*). Ni atom in site 8*j* resulting from Ni in site 2*c* in the small cell is allowed to move along *x* and *y* coordinates. The four interstitial sites for deuterium are split into nine positions, the occupancy of which was refined. The refinement of deuterium atom coordinates does not result in a significant improvement of the reliability factors, therefore they were not allowed to vary during the final stage of the refinement and were kept to their ideal positions. Final refinement results are reported in Table 3, Rietveld plot is presented in Fig. 5.

## 4. Discussion

A complete solid solution is observed between $LaNi_5$ and $LaPt_5$. However, as shown in Fig. 2, the substitution of nickel by platinum is not homogeneous on the two sites. Platinum tends to substitute on site 3*g* as usual for large atoms in $LaNi_5$ (e.g., Sn [8], Al [9]) because of larger space available. For $x = 3$, site 3*g* is almost entirely occupied by platinum leading to the so-called $PrNi_2Al_3$ structure type [10]. For $x > 3$, site 2*c* starts to be filled. The preferential occupancy of platinum can be represented as in Fig. 6 where it is compared to other substitutions. Similar to Al and Sn, and contrary to Cu or Co, Pt occupies preferentially site 3*g*. However, similar to Cu and Co, and contrary to Al and Sn which present limited substitution ranges (respectively up to $x = 1.25$ and 0.5), Pt can be substituted completely with Ni. Platinum offers the nearly unique possibility to study a substituting element both close to nickel from an electronic point of view and far from the size point of view. Its behavior allows concluding that, while the similarity of the electronic properties is the dominant effect leading to the presence of a complete solid solution, the difference in atomic size is the relevant character determining the preferential substitution site.

Table 3
Results of the powder neutron diffraction refinement of $LaNi_{4.25}Pt_{0.75}D_{2.61}$

| | |
|---|---|
| Nominal composition | $LaNi_{4.25}Pt_{0.75}D_{2.61}$ |
| Space group | *Ibam* |
| $a$ (Å) ($\Delta a/a$ (%)) | 9.089 (1) (+3.2%) |
| $b$ (Å) ($\Delta b/b$ (%)) | 5.272 (1) (+3.7%) |
| $c$ (Å) ($\Delta c/c$ (%)) | 8.145 (1) (+1.2%) |
| $V$ (Å$^3$) ($\Delta V/V$ (%)) | 390.3 (1) (+8.3%) |

| Atom | Site | $x$ | $y$ | $z$ | B (Å$^2$) | Occupancy (atom/f.u.) |
|---|---|---|---|---|---|---|
| La | 4*c* | 0 | 0 | 0 | 1.52(5) | 1 |
| Ni | 8*j* | 0.342(1) | 0.028(1) | 0 | 1.45(3) | 2 |
| Ni | 8*e* | 1/4 | 1/4 | 1/4 | 1.03(2) | 1.5 |
| Pt | | | | | | 0.5 |
| Ni | 4*b* | 1/2 | 0 | 1/4 | 1.03(2) | 0.75 |
| Pt | | | | | | 0.25 |
| $D_1$ | 16*k* | 0.330 | 0.000 | 0.190 | 2.1(2) | 0.04(2) |
| $D_{2,1}$ | 16*k* | 0.430 | 0.290 | 0.250 | 2.1(2) | 0.64(4) |
| $D_{2,2}$ | 8*f* | 0.860 | 0 | 1/4 | 2.1(2) | 0.37(4) |
| $D_{3,1}$ | 16*k* | 0.735 | 0.265 | 0.032 | 2.1(2) | 0.27(6) |
| $D_{3,2}$ | 16*k* | 0.500 | 0.030 | 0.032 | 2.1(2) | 0.58(3) |
| $D_{3,3}$ | 16*k* | 0.265 | 0.265 | 0.032 | 2.1(2) | 0.33(6) |
| $D_{4,1}$ | 16*k* | 0.395 | 0.185 | 0.165 | 2.1(2) | 0 |
| $D_{4,2}$ | 16*k* | 0.790 | 0.000 | 0.165 | 2.1(2) | 0 |
| $D_{4,3}$ | 16*k* | 0.395 | 0.815 | 0.165 | 2.1(2) | 0.35(3) |
| D total (atom/f.u.) | 2.58(28) | | | | | |
| $\chi^2$ | 10.2 | | | | | |
| $R_{Bragg}$ (%) | 6.1 | | | | | |

For easy comparison of the occupancy factors, their value in atom/cell has been divided by $Z = 4$.

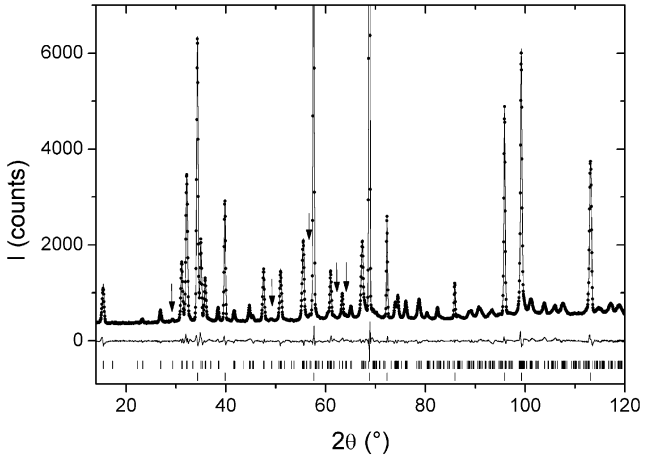


Fig. 5. Neutron diffraction Rietveld refinement pattern of $LaNi_{4.25}Pt_{0.75}D_{2.61}$ under 97.6 bar $D_2$. The observed pattern (dots), the calculated curve (line), the difference curve (line below) and the reflection positions (vertical bars) are plotted. The second phase corresponds to the austenitic stainless-steel container. The arrows indicate the superstructure lines.

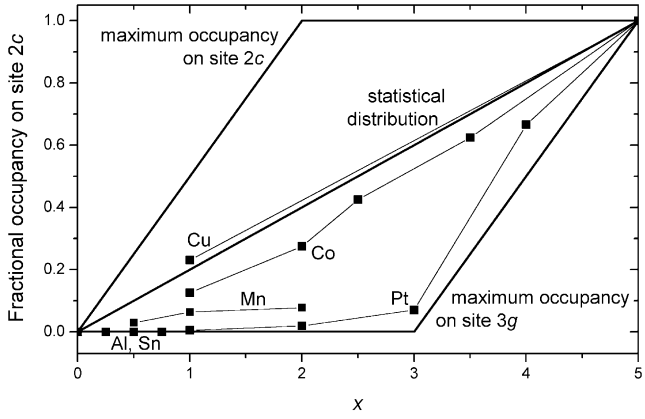


Fig. 6. Fractional occupancy on site 2*c* characterizing the preferential substitution by atom $M$ in $LaNi_{5-x}M_x$ compounds ($M$ = Pt (this work), Al [9], Sn [8], Mn [23], Co [24], Cu [25]). Full lines represent the maximum occupancy on sites 2*c* and 3*g*, and a statistical distribution on the two sites, respectively.

The lattice parameters show an unusual behavior for a solid solution. Contrary to the cell volume which increases with a perfectly linear law, the $a$ parameter increases more than the $c$ parameter for $x<3$, the opposite being observed for $x>3$ resulting in a V shape for the $c/a$ ratio as can be observed in Fig. 1. This is a direct consequence of the two-step replacement of nickel by platinum. From geometrical considerations [11,12], it is observed that the $a$ parameter depends more strongly on the average radius of the atoms occupying site 3*g*, the increase of which is more pronounced for $x<3$ when Pt substitutes on this site and less pronounced for $x>3$, resulting in a nearly constant $a$ parameter. On the contrary, the $c$ parameter depends more on the average radius of the atoms occupying site 2*c* which increases only when $x>3$.

Weisman et al. [13] have already observed the solid solution behavior between $LaNi_5$ and $LaPt_5$ and the same trend for the lattice parameter variation. They have studied the platinum distribution by NMR spectroscopy and found also Pt preferential substitution on site 3*g*. However, we believe that our results from Rietveld refinement of powder X-ray diffraction data due to the high contrast between Pt ($Z = 78$) and Ni ($Z = 28$) are more accurate.

The symmetry decrease observed for $LaNi_{4.75}Pt_{0.25}D_{5.23}$ from *P6/mmm* to *P6mm* is identical to the one occurring in $LaNi_5D_{5.0}$ [14] and $LaNi_{4.8}Sn_{0.2}D_{6.1}$ [8] and has already been discussed in these references. It consists in the splitting of three of the four interstitial sites with distinct occupancies for each of the two sites of the pairs. The symmetry decrease should be related to the weak substitution ratio $x$ rather than to a high deuterium concentration since deuterium does not order in $LaNi_{4.6}Sn_{0.4}D_{5.8}$ whereas it does in $LaNi_{4.75}Pt_{0.25}D_{5.23}$. The ordering in the platinum compound is found to be quite significant since the occupancy parameter of sites $D_{1,1}$, $D_{3,2}$ and $D_{4,1}$ are close to zero.

The supercell found in the case of $LaNi_{4.25}Pt_{0.75}D_{2.61}$ is the same as the one evidenced for $RCo_5D_{2.9}$ ($R$ = Pr, Nd) [15] and $CaNi_5D_y$ ($y = 0.9$, 4.8) [16]. In those two studies, the space group *Im2m* was chosen, but it was not clear whether the presence of additional lines justified the choice of this low symmetry. In our case, clearly no lines were breaking the extinction rules of *Ibam* which is the subgroup of *P6/mmm* with the highest symmetry in the considered cell. In addition, the refinement in this space group yields satisfactory description of the intensities of the superstructure lines (except for the one at 1.197 Å), exact description of the deuterium content, the lowest reliability factor, with the smallest number of parameters. However, given the complexity of the problem (the refinement in *Im2m* involves the refinement of 19 deuterium occupancy parameters and possible 63 atomic positions), it cannot be excluded that the given solution is only an average of a more complex structure.

Ordered displacement of Ni in site 8*j* as regards its ideal position ((1/3,0,0) corresponding to site 2*c* in *P6/mmm*) is evidenced, as could be expected from a preliminary refinement in *P6/mmm* space group which yielded high anisotropic displacement parameters for this atom. The only displacement of this atom is responsible for the largest part of the superstructure line intensities and further refinement of the deuterium occupancies only weakly improves the reliability factor (from $R_{Bragg} = 6.3\%$ to 6.1%). The other metal atoms are fixed by the symmetry of *Ibam* space group. It is possible that the strong increase of the *a* parameter of the hexagonal cell induced by platinum substitution in site 3*g* allows a strong relaxation of the Ni atom in site 2*c* when deuterium is inserted. However, such phenomenon was not observed in Al substituted compounds which present the same feature of a large atom substituting in site 3*g*.

As far as the deuterium sites are concerned, site $D_1$ is found to be almost empty. Site $D_2$ is split into two distinct positions, and $D_3$ into three. In both cases, the refined occupancy ratios are similar between the split sites. Only the three sites resulting from site $D_4$ splitting show a different behavior, since two of them are found to be unoccupied. When it was performed, the refinement of the $z$ coordinates of sites $D_{31}$, $D_{32}$ and $D_{33}$ indicate that those sites are clearly distinct from the octahedral sites related to site 3*f* in the hexagonal cell. A refinement constraining deuterium atoms in this latter site invariably leads to unacceptable values of the displacement parameter of D atoms. This result contrasts with the assumption made by Kuijpers and Loopstra [15] and Yoshikawa et al. [16] in the refinement of $RCo_5D_{2.9}$ and $CaNi_5D_y$, that this latter site should be occupied.

Clearly, no links can be established between the partial ordering occurring in $LaNi_{4.75}Pt_{0.25}D_{5.23}$ and the superstructure observed in $LaNi_{4.25}Pt_{0.75}D_{2.61}$, especially because *Ibam* is not a subgroup of *P6mm*. In one case, strongly different deuterium occupancies were refined, while, in the second case the superstructure is mainly related to the displacement of Ni in position 2*c* of the parent cell. It is worth noting that in $LaNi_{4.25}Pt_{0.75}D_{2.61}$, the displacement parameter of this atom (in position 2*b* in *P6mm*) was already quite high ($B = 2.05$ Å), though no superstructure lines were observed. In both cases, the deuterium content refined is in excellent agreement with the composition measured by the volumetric measurement. The capacity decrease observed in the pressure–composition curves in Fig. 3 is explained by a regular decrease of the occupancies for all the insertion sites. Platinum drastically reduces the hydrogen capacity in a more pronounced manner than any known substituting element in $LaNi_5$ does.

Finally, the main and less expected effect of platinum substitution is to increase the plateau pressure contrary to the usual trend observed in $LaNi_5$ substituted compounds (but also for most hydride forming intermetallic compounds) for which any increase of the cell volume is accompanied by a decrease of the hydrogen absorption plateau pressure. Fig. 7 shows this behavior, for several substituting elements. For most of them (rare earths on La site, Mn, Al, Co on Ni sites), the plateau pressure logarithm decreases as a function of the cell volume following a unique linear law. Some others (Cu, Fe, Sn on Ni sites) follow another but still decreasing linear law. The behavior of platinum on Ni sites is unique. It had been already pointed out by Takeshita et al. [2] that $LaPt_5$ had a high plateau pressure of 200 bar at room temperature. Our study shows that the

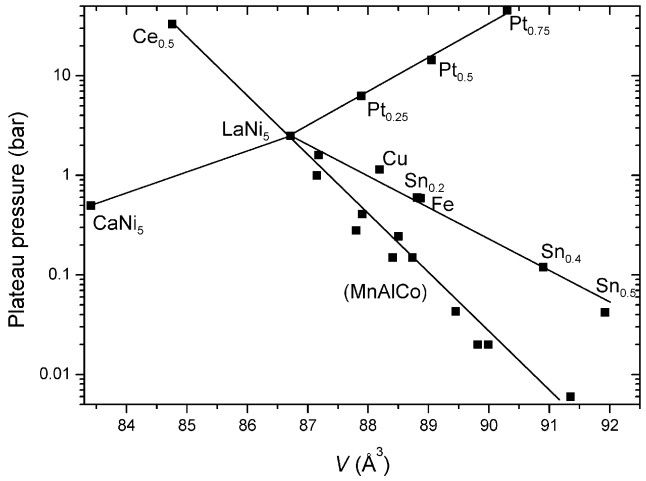


Fig. 7. Plateau pressure at 25°C as a function of the cell volume for $La_{1-y}R_yNi_{5-x}M_x$ compounds ($R$ = Ca, Ce, $M$ = Al, Co, Cu, Fe, Mn, Pt, Sn) (from Refs. [8,26,27]).

increase of the plateau pressure occurs even at the lowest platinum content and in a more pronounced manner than expected by a linear interpolation since an extrapolation of our data would result in a plateau pressure of $10^9$ bar for $LaPt_5$.

The symmetry decrease due to the partial ordering in $LaNi_{4.75}Pt_{0.25}D_{5.23}$ has already been observed for a tin substituted compound. This behavior cannot account for the platinum anomaly. The case of $LaNi_{4.25}Pt_{0.75}D_{2.61}$ is more interesting since the displacement of one of the metal atoms is observed and the additional energy related to this move, and the modification of the site coordinations could possibly account for the increase of the plateau pressure. Even more striking is the fact that $CaNi_5$, the deuteride of which presents the same kind of superstructure, follows the same anomalous law as Pt compounds as can be inferred from Fig. 7.

Interestingly, a similar effect of hydride destabililization has already been observed in $Pd_{1-x}Pt_x$–$H_2$ system. It has been tentatively explained either by lower compressibility of platinum which would contradict the cell expansion induced by hydrogen insertion [17] or by an important broadening of the valence band [18]. It can be also explained by the repulsive character of Pt towards hydrogen since this element does not form any hydride at $9 \times 10^5$ bar (V.E. Antonov, personal communication) while Ni forms NiH at $6 \times 10^3$ bar [19]. In the case of $LaNi_{5-x}Pt_x$–$H_2$ system, decreasing compressibility values as regards $LaNi_5$ have been evaluated from specific heat measurements as a function of $x$ [2, 20] and could account for the peculiar behavior observed if one assumes that a metal lattice should be soft enough to accommodate hydrogen. In addition, recent measurements [21] indicate far lower free enthalpy of formation for $LaPt_5$ (−390 kJ/mol) as compared to $LaNi_5$ (−144 kJ/mol). According to the so-called rule of the reversed stability [22], the more stable is the intermetallic compound, the less stable should be the hydride. The exceptional stability of $LaPt_5$ could therefore explain the peculiar instability of its hydride and, by extension, of the hydrides formed by $LaNi_{5-x}Pt_x$ compounds.

## 5. Conclusion

The system $LaNi_{5-x}Pt_x$–$H_2$ was investigated in detail. From a metallurgical point of view, a continuous solid solution exists between $LaNi_5$ and $LaPt_5$ as a consequence of similar electronic properties for Ni and Pt. However, because of different atomic sizes, the substitution of platinum is not homogeneous on the two nickel sites and leads to a nearly complete ordering at the composition $LaNi_2Pt_3$ responsible for the exceptional brittleness of this alloy. With platinum content the hydrogen capacity is shown to drastically decrease. Less expectedly, the plateau pressure was shown to increase strongly with platinum substitution. This anomaly is explained by three possibly correlated reasons: peculiar structural feature of the hydride, decrease of the compressibility and increase of the enthalpy of formation of the intermetallic compound.

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