Compressibility and thermal expansion of LaNi$_5$ and its substitutional derivatives (LaNi$_{5-x}$M$_x$; M=Mn, Al, Co)


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Received 8 June 2004; received in revised form 10 August 2004; accepted 18 August 2004
Available online 18 October 2004

Abstract

The elastic properties of LaNi$_5$ and related substitutional derivatives (LaNi$_{4.6}$Mn$_{0.4}$, LaNi$_{4.7}$Al$_{0.3}$, LaNi$_{4.25}$Co$_{0.75}$ and LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$) are investigated by means of room temperature compressibility and low-temperature thermal expansion (both studied by powder diffraction methods). Anisotropy of the compressibility and thermal expansion coefficients has been evidenced. The extent of this anisotropy changes, depending on the substituting element. A softening of the lattice accompanies also the substitution. These findings have been tentatively related to the nature and the quantity of the defects generated during hydride formation by those compounds.

Keywords: A. Rare-earth intermetallics; B. Elastic properties; B. Hydrogen storage; D. Defects: dislocation geometry and arrangement; F. Diffraction

1. Introduction

LaNi$_5$ intermetallic compound (CaCu$_5$ structure type, P6/mmm) and its substituted derivatives, due to their outstanding ability to react reversibly with hydrogen, have been widely used for hydrogen gas storage, as well as for electrochemical storage giving rise to the industrial application of nickel–metal hydride batteries. In these compounds, hydride formation takes place by means of a discrete phase transition between a hydrogen-poor (0.1 H per metal atom) solid solution and the hydrogen-rich hydride (0.6–1 H per metal atom). Binary LaNi$_5$ accepts wide ranges of pseudo-binary substitutions yielding important changes in the related hydride properties. In previous work, we have investigated the nature and density of the defects created during hydrogen absorption–desorption cycling in LaNi$_5$ and substituted compounds. This was made by means of the analysis of the anisotropic diffraction line broadening observed in high resolution synchrotron powder diffraction patterns [1,2]. The study of the defects generated is of primary importance to understand the ageing properties of the compounds. The data were explained considering the two different dislocation systems E1 (1/3 < −2110 > (0001)) and E2 (1/3 < −2110 > (0 − 110)), both with Burgers vector a, gliding in basal or prismatic planes, respectively. Depending on the substitution, two main effects were observed: (i) a change of the glide system from prismatic (LaNi$_5$, LaNi$_{4.25}$Co$_{0.75}$) to basal (Mn-substituted compounds) and (ii) a reduction of the dislocation density from a very high content (≈4×10$^{11}$ cm$^{-2}$) (LaNi$_5$, LaNi$_{4.25}$Co$_{0.75}$, manganese substituted compounds) to a hardly detectable quantity with the line broadening technique (LaNi$_{4.7}$Al$_{0.3}$, LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$). The change of the glide system has been explained by the change of the hydride phase precipitate shape, which develops coherently (i.e. with the same crystal orientation) in the matrix of the hydrogen-poor solid solution during absorption. The origin of this change remains unknown. On the other hand, it is believed that the creation of a high density of defects is induced by the huge discrete lattice volume expansion between the two phases (up to 22.4%). However, our systematic study [3] failed to explain by this unique parameter the differences regarding defect densities between the different substituted compounds. It was therefore postulated that, in addition to
this parameter, the different elastic properties of the intermetallic compounds could explain their distinct behaviours. We investigate these latter properties in the present work.

The extreme brittleness of the compounds makes them inappropriate for traction or compression methods. In addition, the presence of voids and cracks in polycrystalline samples and the difficulty to obtain large single crystals explain the fact that only rare studies of the elastic properties were performed by the ultrasonic method ([4] (single crystal), [5] (polycrystal)). Therefore, high-pressure compressibility and low-temperature thermal expansion powder diffraction measurements were performed. Moreover, diffraction methods present the outstanding advantage to provide crystallographic direction sensitive results.

2. Experimental

As detailed in Ref. [1], the intermetallic compounds were prepared by induction melting of the pure elements followed by a suitable annealing. Their single-phase character and compositional homogeneity were checked by conventional X-ray diffraction and electron probe micro-analysis. High-pressure compressibility measurements were performed at the ESRF, on ID30 beamline in a diamond anvil cell at room temperature. The diffraction was obtained in angle dispersive mode \( lZ0.41683\ \text{Å} \), the data were collected on an imaging plate and integrated using Fit2D software [6]. The lattice parameters were obtained by the Rietveld method using Fullprof software [7]. The second phase corresponding to the pressure medium (N\(_2\)) was not taken into account in the refinements. The cell volumes were fitted using a Birch–Murnaghan equation of the third order (Eq. (1)) with EOSFIT5.2 software [8], and the bulk modulus at zero pressure \( B \) and its pressure derivative \( B' \) have been obtained.

\[
P = \frac{3}{2} B \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \left( \frac{V_0}{V} \right)^{5/3} \times \left[ 1 + \frac{3}{4}(B' - 4) \left( \frac{V_0}{V} \right)^{2/3} \right] - 1 \]
\]

Axial compressibilities \( \kappa_a \) and \( \kappa_c \) are more reliably obtained by fitting an equation of states to the lattice parameters than by extrapolating the lattice parameter derivatives to zero pressure. This is automatically performed in EOSFIT5.2 software by using Eq. (1) and substituting \( a^3 \) or \( c^3 \) for the cell volume. Axis related moduli \( B_a \) and \( B_c \) are then obtained from which the axial compressibilities are calculated by the following equations:

\[
\kappa_a = 1/(3B_a); \quad \kappa_c = 1/(3B_c)
\]

The low-temperature thermal expansion measurements were performed on the Swiss Norwegian Beamline of the ESRF. A capillary with diameter 0.3 mm was filled with the powder samples and cooled by a cold nitrogen gas stream (Oxford Cryosystems, series 600). The powder patterns \((lZ0.70165\ \text{Å}, \text{calibrated by a silicon NIST standard})\) were collected with an imaging plate and integrated with the Fit2D software [6]. The lattice parameters were obtained by the Rietveld method using Fullprof software [7]. The volume expansion coefficient \( \beta \) and the linear expansion coefficients \( \alpha_a \) along the \( a \)- and \( c \)-directions are defined as

\[
\beta = 1/V_T(\partial V/\partial T)_T
\]

\[
\alpha_a = 1/a_T(\partial a/\partial T)_T; \quad \alpha_c = 1/c_T(\partial c/\partial T)_T
\]
The dependence of the lattice parameters on the temperature is linear in the temperature interval 235–295 K. \( \alpha \) and \( \beta \) coefficients can be well approximated by fitting a linear law in this region. At lower temperatures, the decrease of the expansion coefficients, especially along the \( c \)-direction was observed in all the samples.

### 3. Results and discussion

Five samples have been studied which present different behaviours towards dislocation formation [1,2]: LaNi\(_5\), LaNi\(_{4.8}\)Mn\(_{0.4}\), LaNi\(_{4.7}\)Al\(_{0.3}\), LaNi\(_{4.25}\)Co\(_{0.75}\) and LaNi\(_{3.55}\)Mn\(_{0.4}\)Al\(_{0.3}\)Co\(_{0.75}\). Compressibility and low-temperature thermal expansion data showing the variation of the lattice parameters as a function of pressure or temperature have been plotted in Figs. 1 and 2, respectively. The parameters resulting from those measurements (linear compression parameters, bulk modulus and pressure derivative, linear and volume thermal expansion parameters) have been compiled in Table 1 for the five compounds investigated.

#### 3.1. Discussion of the compressibility and thermal expansion results

It can be observed from the linear compressibility and thermal expansion coefficients obtained from Figs. 1 and 2 that the \( \alpha \)-direction is softer than the \( c \)-direction in all the compounds studied. Besides, a softening of the lattice is observed to accompany the substitution of the binary compound LaNi\(_5\). This can be observed from the decrease of the bulk modulus for Al and Mn single substituted compounds. This is in agreement with the fact that Al and Mn are softer metals than nickel. The decrease is even more pronounced for the sample in which the three substituting elements (Mn, Al and Co) are combined (three-substituted compound) demonstrating an additive behaviour of the substitution effects. Depending on the substitution, the anisotropy of the elastic properties, as measured by

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a_0 ) (Å)</th>
<th>( c_0 ) (Å)</th>
<th>( V_0 ) (Å(^3))</th>
<th>( B ) (GPa)</th>
<th>( B' )</th>
<th>( \kappa_a ) (10(^{-3}) GPa(^{-1}))</th>
<th>( \kappa_c ) (10(^{-3}) GPa(^{-1}))</th>
<th>( \alpha_a ) (10(^{-5}) K(^{-1}))</th>
<th>( \alpha_c ) (10(^{-5}) K(^{-1}))</th>
<th>( \beta ) (10(^{-5}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi(_5)</td>
<td>5.0178</td>
<td>3.9817</td>
<td>86.821</td>
<td>123.6(8)</td>
<td>5.0(1)</td>
<td>2.87(2)</td>
<td>2.36(3)</td>
<td>1.23(8)</td>
<td>1.23(9)</td>
<td>3.7(1)</td>
</tr>
<tr>
<td>LaNi(<em>{4.25})Co(</em>{0.75})</td>
<td>5.0288</td>
<td>3.9835</td>
<td>87.242</td>
<td>122.4(16)</td>
<td>4.8(3)</td>
<td>2.92(4)</td>
<td>2.34(3)</td>
<td>1.27(3)</td>
<td>1.14(2)</td>
<td>3.67(6)</td>
</tr>
<tr>
<td>LaNi(<em>{4.7})Al(</em>{0.3})</td>
<td>5.0339</td>
<td>4.0080</td>
<td>87.956</td>
<td>119.5(5)</td>
<td>4.9(fixed)</td>
<td>2.98(2)</td>
<td>2.41(1)</td>
<td>1.11(1)</td>
<td>1.06(1)</td>
<td>3.28(3)</td>
</tr>
<tr>
<td>LaNi(<em>{4.6})Mn(</em>{0.4})</td>
<td>5.0453</td>
<td>4.0151</td>
<td>88.512</td>
<td>116.6(7)</td>
<td>4.7(1)</td>
<td>3.00(2)</td>
<td>2.59(7)</td>
<td>1.16(2)</td>
<td>1.12(1)</td>
<td>3.45(3)</td>
</tr>
<tr>
<td>LaNi(<em>{3.55})Mn(</em>{0.4})Al(<em>{0.3})Co(</em>{0.75})</td>
<td>5.0653</td>
<td>4.0436</td>
<td>89.974</td>
<td>109.8(11)</td>
<td>4.9(1)</td>
<td>3.25(3)</td>
<td>2.61(5)</td>
<td>1.326(5)</td>
<td>1.04(1)</td>
<td>3.69(2)</td>
</tr>
</tbody>
</table>

![Fig. 2. Relative lattice parameter variation as a function of decreasing temperature in the low-temperature thermal expansion experiment.](image-url)
the linear compressibility and thermal expansion coefficients, is observed to change as can be inferred from Table 1 and Figs. 3 and 4 which plot normalized \(\frac{c}{a}\) as a function of pressure and temperature. To make a comparison between the two techniques used in this work, it is worthy to note that the dependence of the lattice parameters on the pressure and on the temperature shows a similar trend for each substituting element though the relative changes of the lattice parameters is far less extended in the latter case. The compounds can be classified with both techniques from more anisotropic (LaNi\(_{3.55}\)Mn\(_{0.4}\)Al\(_{0.3}\)Co\(_{0.75}\)) to less anisotropic (LaNi\(_{4.6}\)Mn\(_{0.4}\)).

The bulk modulus values can be compared with the ones reported in the literature. Our value for LaNi\(_{5}\) (123.6 GPa) is in good agreement with the value of 126.6 GPa calculated from the elastic constants \(C_{ij}\) obtained by ultrasonic measurements on a single crystal [4] using

\[
B = \frac{[(C_{11} + C_{12})C_{33} - 2C_{13}^2]/(C_{11} + 2C_{33} + C_{12} - 4C_{13})}{(5)}
\]

The bulk modulus values of LaNi\(_{5}\) and LaNi\(_{4.7}\)Al\(_{0.3}\) (119.5 GPa) are in relative agreement with those of LaNi\(_{5}\) (131.4 GPa) and of LaNi\(_{4.75}\)Al\(_{0.25}\) (127.2 GPa) obtained from ultrasonic measurements on polycrystalline samples (values not corrected for the porosity) by Bereznitsky et al. [5].

The anisotropy of the elastic properties of LaNi\(_{5}\) was noted by Tanaka et al. [4] (\(C_{11} = 190\) GPa, \(C_{33} = 230\) GPa). The measured values of the zero pressure axial compressibilities \((\kappa_a = 2.87 \times 10^{-3}\) GPa\(^{-1}\), \(\kappa_c = 2.36 \times 10^{-3}\) GPa\(^{-1}\)) for LaNi\(_{5}\) are in excellent agreement with the values \(\kappa_a = 2.8 \times 10^{-3}\) GPa\(^{-1}\), \(\kappa_c = 2.3 \times 10^{-3}\) GPa\(^{-1}\) calculated from the single crystal elastic constants by using

\[
\kappa_a = \frac{(C_{33} - C_{13})/[((C_{11} + C_{12})C_{33} - 2C_{13}^2]} \quad (6)
\]

\[
\kappa_c = \frac{(C_{11} + C_{12} - 2C_{13})/[((C_{11} + C_{12})C_{33} - 2C_{13}^2]} \quad (7)
\]

Finally, a correlation can be established between the bulk modulus and the cell volume (Fig. 5). From this plot, we can...
deduce that the variations of the elastic properties of the compounds with the CaCu5 structure type are determined to a large extent by the bond lengths. The longer are the interatomic distances the softer is the compound. This is a more general analysis than the one developed by Takeshita et al. [9] who considered only the distances between the atoms in position 3g. This behaviour is in agreement with what was observed in the systems LaNi5−xAlx and LaNi5−xSnx [10] and what is observed in the Laves phase compounds Zr(Fe1−xAlx)2 as a function of x both in the C14 and C15 regions [11].

3.2. Relationship with dislocation formation

The relationship between the parameters related to the elastic properties and the tendency to form dislocations when hydrides are precipitated in the compound are difficult to draw for at least two reasons: (i) only hydrogen-free intermetallic compounds were studied and (ii) only the parameters related to the elastic properties and not to the plastic deformation were studied. However, the comparison between the different samples seems to be meaningful.

By calculation of the elastic energy (as derived from the measurement of the elastic constants of LaNi5) associated with the precipitation of a hydride phase coherently growing in the intermetallic matrix [4] a conclusion was made, that a precipitation along the c-direction should be favoured by the fact that this direction is harder. This conclusion was found to be in a good agreement with the idea that a high concentration of E2 type (Burgers vector a, prismatic) dislocations (case of LaNi5) should be favoured by a c-oriented needle-like growth of the hydride precipitate [1,2], and with the observed shape of grains of hydrogen cycled compounds [3,12] showing a preferential decrement behaviour along the c-axis.

Following the same reasoning, it can be inferred that a compound showing less anisotropy of the elastic properties would give rise to a more isotropic precipitate growth involving the activation of other dislocation systems, like E1 (Burgers vector a, prismatic) or other types with Burgers vector c. Such growth type was described as being responsible for the presence of two dislocation systems in Mn-substituted compounds in our previous work [1,2]. Less anisotropic compressibility and thermal expansion behaviour of LaNi5−xMnx0.4 compared to other compounds found in this work (Figs. 3 and 4) seem to confirm this hypothesis.

The large softening of the lattice evidenced in the case of the three-substituted compound could be responsible for larger yield strength and accordingly higher resistance to hydrogen induced dislocation formation. This assumption awaits the additional measurements of plastic deformation parameters. Finally, a recent study of the diffraction line broadening after hydrogen cycling in Laves phase compounds has shown that the strains induced were larger in the C14 than in the C15 structures [13,14]. As a softer lattice is expected to occur in the C15 structure, these results would be a confirmation of our hypothesis.

Acknowledgements

The authors wish to thank M. Hanfland from ID 30 beamline, and the staff of the Swiss Norwegian beamline at the ESRF, for assistance during the synchrotron measurements.

References