Correlations between stacked structures and weak itinerant magnetic properties of La$_{2-x}$Y$_x$Ni$_7$ compounds

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Received 20 April 2020, revised 8 June 2020
Accepted for publication 16 June 2020
Published 17 July 2020

Abstract

Hexagonal La$_2$Ni$_7$ and rhombohedral Y$_2$Ni$_7$ are weak itinerant antiferromagnet (wAFM) and ferromagnet (wFM), respectively. To follow the evolution between these two compounds, the crystal structure and magnetic properties of $A_2B_7$ intermetallic compounds ($A =$ La, Y, $B =$ Ni) have been investigated combining x-ray powder diffraction and magnetic measurements. The La$_{2-x}$Y$_x$Ni$_7$ intermetallic compounds with $0 \leq x \leq 1$ crystallize in the hexagonal Ce$_2$Ni$_7$-type structure with Y preferentially located in the $[A_2B_4]$ units. The compounds with larger Y content ($1.2 \leq x < 2$) crystallize in both hexagonal and rhombohedral (Gd$_2$Co$_7$-type) structures with a substitution of Y for La in both $[A_2B_4]$ and $[AB_5]$ units. Y$_2$Ni$_7$ crystallizes in the rhombohedral structure only. The average cell volume decreases linearly versus Y content, whereas the $c/a$ ratio presents a minimum at $x = 1$ due to geometric constrains. The magnetic properties are strongly dependent on the structure type and the Y content. La$_2$Ni$_7$ displays a complex metamagnetic behavior with split AFM peaks. Compounds with $x = 0.25$ and 0.5 display a wAFM ground state and two metamagnetic transitions, the first one toward an intermediate wAFM state and the second one toward a FM state. $T_N$ and the second critical field $\mu_0 H_c^2$ increase with the Y content, indicating a stabilization of the AFM state. LaYNi$_7$, which is as the boundary between the two structure types, presents a very wFM state at low field and an AFM state as the applied field increases. All the compounds with $x > 1$, and which contains a rhombohedral phase are wFM with $T_C = 53(2)$ K. In addition to the experimental studies, first principles calculations using spin polarization have been performed to interpret the evolution of structural phase stability for $0 \leq x \leq 2$.

Keywords: intermetallic, crystal structure, weak itinerant magnetism, metamagnetism, first principles calculations

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
1. Introduction

$A_2Ni_7$ compounds (A = rare earth) have raised interest for their fundamental physical properties [1–3] as well as their applications as hydrogen storage materials [4–6] and negative electrodes in Ni–MH batteries [7–11]. $A_2Ni_7$ intermetallic compounds crystallize in two polymorphic crystal structures which are either hexagonal (Ce$_2$Ni$_7$-type, P6$_3$/mmc) or rhombohedral (Gd$_2$Co$_7$-type, R$-3m$) depending on the stacking of the [A$B_3$] and [AB$_3$] units along the c axis ($B = Ni$) [1]. The hexagonal (2$H$) structure is favored for intermetallic compounds with large A elements (La, Ce) and the rhombohedral (3$R$) for smaller A ones (Ho, Er, Y) [1, 3]. A mixture of both polymorphs is obtained for the compounds which contain intermediate A size elements. However, the annealing temperature can also be used to tune the weight percentage of each phase [1, 12].

Their magnetic properties have been investigated [13], and particular interest has been raised on the peculiar itinerant magnetic properties of La$_2$Ni$_7$ [12, 14–17] and Y$_2$Ni$_7$ [18–23] which both contain non-magnetic A elements. Weak itinerant magnetism is related to the electronic structure and the small magnetic moment arises from the exchange splitting of the bands near the Fermi level. Weak itinerant magnets are close to the boundary between magnetic and non-magnetic state and a small structural variation can induce large changes in both electronic and magnetic properties. Such magnetic instabilities have been observed and studied in other weak ferromagnets (wFM) as Ni$_3$Al [24–26], Fe$_2$N [27, 28], AsNCl$_3$ [29], CrAlGe [30] or weak antiferromagnets (wAFM) like TiAu [31] and UN [32]. The weak itinerant magnetism is often associated to large spin fluctuations. For example, although Ni$_3$Al and Ni$_3$Ga have close electronic structures, they differ by their magnetic properties: Ni$_3$Al is a weak itinerant ferromagnet, whereas Ni$_3$Ga is a paramagnet [26, 33]. This difference has been attributed to the larger spin fluctuations in Ni$_3$Ga [26].

Earlier reported magnetic investigations on hexagonal La$_2$Ni$_7$ have shown that the ground state is a weak itinerant antiferromagnet with a Néel temperature $T_N = 50$ K at low field [12, 34]. Multiple field-induced metamagnetic transitions from wAFM state toward a weak itinerant ferromagnetic state have been observed. The transition fields-temperature phase diagram reveals the existence of different magnetic transitions below 60 K [14–17]. Parker et al [12] were able to obtain a sample containing both hexagonal and rhombohedral structures after annealing at 873 K, and found a wFM behavior with a Curie temperature $T_C = 70$ K associated to rhombohedral La$_2$Ni$_7$. In both hexagonal and rhombohedral phases, the saturation magnetization $\mu_{sat}$ remains weak (0.11 and 0.086 $\mu_B$/Ni respectively), whereas the effective Ni moment determined by a Curie Weiss law in the paramagnetic range varies between 0.9 and 1.04 $\mu_B$/Ni. In a recent theoretical work, an hexagonal AFM structure has been proposed, described by two FM unit blocks of opposite Ni spin sign separated by a non-magnetic layer at $z = 0$ and $\lambda / \gamma$ [35]. This AFM structure and the corresponding FM structure are more stable with Ni moments parallel to the c axis. The Ni moment magnitude depends on the neighboring atoms, it is minimum in the [A$B_3$] unit and increase to a maximum at the interface between two [AB$_3$] units.

Rhombohedral Y$_2$Ni$_7$ has been described as a wFM with $T_C = 53$ to 60 K and $\mu_{sat} = 0.06$ to 0.08 $\mu_B$/Ni, depending on the Ni content (Y$_2$Ni$_{6.7}$ to Y$_2$Ni$_7$) [19–22, 36]. A theoretical study of its electronic density has been undertaken to explain the origin of the itinerant ferromagnetic properties of Y$_2$Ni$_7$ with a very weak Ni moment and a corresponding relatively elevated transition temperature [23]. A sharp and narrow peak is observed in the density of state (DOS) at the Fermi level ($E_F$) leading to a high density of state and stabilizing the spin polarized configuration with a ferromagnetic state.

The influence of partial substitution of Gd for Y [37], Al, Co and Cu for Ni [15, 38, 39] as well as hydrogen insertion [34, 36] has revealed a large sensitivity of the magnetic properties for both La$_2$Ni$_7$ and Y$_2$Ni$_7$ to these chemical substitutions or insertion. However, it appears to have no studies on the properties of intermediate compounds between La$_2$Ni$_7$ and Y$_2$Ni$_7$. Due to the difference of crystal structure (hexagonal/rhombohedral) and itinerant magnetic properties (antiferromagnetic/ferromagnetic) of the binary compounds, it is worth to understand how the change between these different states is occurring: is it continuous or discontinuous, is there any critical Y concentration at which the change of crystal structure occurs? One important question is the correlation between the crystal structure and the magnetic order. In previous DFT calculation study [35], we have found an AFM structure which is compatible with the hexagonal structure, but not with the rhombohedral one. In addition, for hexagonal La$_2$Ni$_7$, both AFM and FM structures have comparable magnetic energy at 0 K, which raises the question of stability range of the AFM state and how it is modified by structural changes.

To answer these questions, we have investigated the structural and magnetic properties of the La$_{2-x}$Y$_x$Ni$_7$ system (0 $\leq x \leq 2$) to follow the evolution from the hexagonal La$_2$Ni$_7$ antiferromagnet toward the rhombohedral Y$_2$Ni$_7$ ferromagnet. Complementary to the experimental study, band structure calculations have been undertaken to interpret the evolution of these properties. This will contribute to determine the key geometric and electronic parameters which drive the change of the physical properties of these compounds.

2. Experimental and calculation conditions

Polycrystalline samples with composition La$_{2-x}$Y$_x$Ni$_7$ (x = 0, 0.25, 0.5, 1, 1.2, 1.4 and 2) were prepared by induction melting under a purified argon atmosphere and annealed 7 days at 1223–1273 K as described in previous work [5]. The samples were annealed at high temperature to get compounds with a single structure type when possible.

The samples were characterized by x-ray diffraction (XRD) using a D8 diffractometer from Bruker with Cu K$_\alpha$ radiation. The XRD patterns were refined using the Fullprof code [40]. Their chemical compositions were analyzed by electron probe microanalysis (EPMA) using an SX100 from Cameca.

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The magnetic measurements were performed on small quantity of sample (bulk piece or powder fixed by a resin) with a physical properties measurement system (Quantum Design PPMS-9) operating from 2 to 300 K, with a maximum applied field of 9 T. The magnetization measurements of La$_{1.75}$Y$_{0.25}$Ni$_7$ and La$_{1.5}$Y$_{0.5}$Ni$_7$ were extended up to 14 T using a commercial vibrating-sample magnetometer (Quantum Design PPMS-14).

The electronic structures were calculated for the ordered compounds La$_2$Ni$_7$ and Y$_2$Ni$_7$ in both hexagonal (H) and rhombohedral (R) symmetries. Since no distinct total energy differences were observed in the non-spin polarized calculations between binaries with R or H structure, the La$_{2-x}$Y$_x$Ni$_7$ compounds with $x = 0, 0.5, 1, 1.5$ and 2 have been only considered in the rhombohedral cell (primitive rhombohedral, not hexagonal for CPU-time saving). In this 18-atoms cell, all ordered kinds of $A$-site configurations have been considered ($6c_1$ and $6c_2$ with half or full substitution of La by Y). This $A$-ordering approximation differs from an ideal solid solution representation where a random distribution is preferable, but is sufficient since our preliminary tests on pseudo-disordered supercells presented similar energetic results that the ordered case [41].

In the frame of the DFT, the pseudo-potential approach using the VASP package [42, 43] was considered by applying the generalized gradient approximation with the PBE functional [44] using a 600 eV cut-off energy and a high $k$-mesh density (grid of $9 \times 9 \times 9$ for the rhombohedral and $21 \times 21 \times 7$ for the hexagonal structure). Preserving the original crystal symmetry, each structure has been fully relaxed with the electronic collinear and non-collinear spin-polarization.

3. Results and discussion

3.1. Structural properties

The A$_2$Ni$_7$ alloys can adopt either the rhombohedral Gd$_2$Co$_7$-type or the hexagonal Ce$_2$Ni$_7$-type structure, as shown in figure 1. Both structures are related to the stacking along the $c$ axis of $[A_2B_1]$ and $[AB_3]$ units according to the rule $[A_2B_4]+n[AB_3]$, where $n$ is an integer. Note that the $[A_2B_1]$ sub-unit will be renamed as $[AB_2]$ for simplicity in the following. The rhombohedral cell (hexagonal description) contains three stacking of two $[AB_3]$ and one $[AB_2]$ units, whereas the hexagonal cell contains only two of them, with a mirror inversion of the $[AB_2]$ units located in the top $[AB_2^1]$. In each cell, the $A$ atoms belong to two different Wyckoff sites (table 1): the $A$ atom belonging to the $[AB_3]$ unit is surrounded by 16 atoms (CN16, with CN for coordination number), whereas the one belonging to the $[AB_2]$ unit is surrounded by 20 atoms (CN20).

The XRD patterns were refined with a single hexagonal structure (Ce$_2$Ni$_7$-type structure) for $x \leq 1$, a mixture of hexagonal and rhombohedral structures for $1 < x < 2$ and a single rhombohedral structure (Gd$_2$Co$_7$-type structures) for $x = 2$ in agreement with [22, 36]. The refined patterns of samples with $x = 0, 0.25, 1, 1.2$ are presented in supplementary material (figure S1 (https://stacks.iop.org/JPCM/32/415804/mmedia)) and the factors of agreement are added in the legend. The crystal structure analysis of rhombohedral Y$_2$Ni$_7$ is presented in details in reference [5]. All the hexagonal compounds are well crystallized, without anisotropic line broadening.

Note that the XRD pattern of La$_{1.75}$Y$_{0.25}$Ni$_7$ displays small additional lines due to 1.4 wt% of cubic LaNi$_2$, whereas that of La$_{0.5}$Y$_{1.2}$Ni$_7$ the few additional lines are refined with 1.7 wt% of Y$_2$O$_3$.

In addition, difference between the calculated and experimental patterns for $x = 1.2$ and 1.4 is observed in the $2\theta$ range between 25 and 35° (inset of figure S1(b)). This difference can be attributed to the existence of microstructural defects. These defects have been interpreted as stacking faults due to some random local variation of $n$ in the stacking of the $[AB_2^1]$ + $n[AB_3]$ units along the $c$ axis. These defects have been clearly observed by HAADF STEM images in La$_{0.65}$Nd$_{0.15}$Mg$_{0.20}$Ni$_{3.5}$ and La$_{0.75}$-0.80Mg$_{0.30}$-0.38Ni$_{3.67}$ alloys [45, 46]. Such defects cannot be considered by classical diffraction analysis as they are not periodic. Indeed, the diffraction patterns show some broadening located between 30 and 35° that are directly related to these stacking faults and that cannot be refined using Fullprof refinement. A more detailed analysis of these stacking faults is under progress with the FAULTS code [47] and will be detailed in a further work, but a first simulation indicates a maximum of 9% of stacking faults in Y$_{1.2}$La$_{0.8}$Ni$_7$. It is important to note that such defects have small incidence on the diffraction patterns as most of the x-ray diffraction peaks are not affected by these stacking faults. Therefore, the full pattern refinement performed with Fullpro fully allows to determine the atomic positions and phase contents.

The cell parameters as well as the chemical compositions determined by EPMA for the La$_{2-x}$Y$_x$Ni$_7$ compounds are summarized in table 2. The evolution of $a$ and $c$ cell parameters, cell volume $V$ and $c/a$ ratio versus Y content is reported in figure 2. The weight percentage of each phase is shown in figure 3(a). For $x = 1.2$ and 1.4, the $aR$ and $aH$ cell parameters are similar, whereas the rhombohedral $cR$ parameter is 3/2 times the hexagonal $cH$ one. The $a$ ($aR$ and $aH$) and $c$ ($cH$ and 2/3 $cR$) cell parameters decrease continuously versus Y content following a second order polynomial law with opposite curvatures (the polynomial coefficients are reported in figure 2). The $c/a$ ratio (hexagonal description) passes through a minimum near $x = 1$, then increases again. For $x < 1$, the $c/a$ ratio follows a power law with a square exponent ($y/c(a) = 0.27(x − 1)^2$). On the other hand, a linear decrease of the reduced cell volume $V/Z$ with $d(V/Z)/dx = 2.97 \AA^3 \; \text{f.u.}^{-1}$ is observed independently of the structure type, in agreement with the Vegard’s law expected for a solid solution (figure 2).

The refined Y occupancy factors and atomic positions for each compound in both hexagonal and rhombohedral structures are reported in table 3. The Y atoms are first substituted to La in the 4$f_1$ site which belongs to the $[AB_3]$ units with a coordination number CN16, where the compounds crystalize in hexagonal structure. For $x \geq 1$, an additional progressive filling of the 4$f_2$ (6$c_1$) sites, belonging to the $[AB_3]$ units (CN20), is observed in both hexagonal and rhombohedral structures (figure 3(b)). The evolution of the $A$–$A$ interatomic distances...
Figure 1. Illustration of the rhombohedral Gd$_2$Co$_7$-type and hexagonal Ce$_2$Ni$_7$-type structures with the coordination spheres of each A Wyckoff sites. The three different A–A interatomic distances ($d_1$, $d_2$, $d_3$) are indicated by arrows.

Table 1. Tabulated atomic positions for A$_2$Ni$_7$ phases in hexagonal (P6$_3$/mmc) and rhombohedral (R-3m) symmetries.

| Hexagonal Ce$_2$Ni$_7$ Type | atom   | Wyckoff | x     | y     | z     | Unit       | Neighbors | CN |
|---------------------------|--------|---------|-------|-------|-------|------------|-----------|-----|
|                           | A$_1$  | 4$f_1$  | 1/3   | 2/3   | 0.5   | [AB$_2$]   | 4A + 12Ni | 16  |
|                           | A$_2$  | 4$f_2$  | 1/3   | 2/3   | 0.667 | [AB$_3$]   | 2A + 18Ni | 20  |
| Ni$_1$                    | 12$k$  | 0.834   | 2$x$  |       | 0.085 | [AB$_2$]/[AB$_3$] | 5A + 7Ni | 12  |
| Ni$_2$                    | 6$h$   | 0.167   | 2$x$  |       | 1/4   | [AB$_2$]   | 4A + 8Ni | 12  |
| Ni$_3$                    | 4$f_3$ | 1/3     | 2/3   |       | 0.167 | [AB$_2$]   | 3A + 9Ni | 12  |
| Ni$_4$                    | 4$e$   | 0       | 0     |       | 0.167 | [AB$_2$]   | 3A + 9Ni | 12  |
| Ni$_5$                    | 2$a$   | 0       | 0     |       | 0     | [AB$_2$]   | 6A + 6Ni | 12  |

| Rhombohedral Gd$_2$Co$_7$ Type | atom   | Wyckoff | x     | y     | z     | Unit       |
|---------------------------|--------|---------|-------|-------|-------|------------|
|                           | A$_1$  | 6$c_1$  | 0     | 0     | 0.056 | [AB$_2$]   |
|                           | A$_2$  | 6$c_2$  | 0     | 0     | 0.167 | [AB$_2$]   |
| Ni$_1$                    | 18$h$  | 0.5     | $-x$  |       | 0.111 | [AB$_2$]/[AB$_1$] |
| Ni$_2$                    | 9$e$   | $1/2$   | 0     |       | 0     | [AB$_2$]   |
| Ni$_3$                    | 6$c_3$ | 0       | 0     |       | 0.278 | [AB$_2$]   |
| Ni$_4$                    | 6$c_4$ | 0       | 0     |       | 0.389 | [AB$_1$]   |
| Ni$_5$                    | 3$b$   | 0       | 0     |       | $1/2$ | [AB$_2$]   |

presented in figure 3(c) can be correlated to the cell parameter variations. First, we observe that the A–A distances are shorter in the [AB$_2$] units ($d_1$) than in the [AB$_3$] units ($d_3$), whereas the distances between two A atoms belonging to each unit type ($d_2$) are intermediate. The short $d_1$ distance decreases more sharply for $x > 1$, whereas the intermediate $d_2$ distance slightly increases. As the atoms belonging to the same [AB$_2$] units are almost in the same ($a$, $b$) plane whereas the A atoms belonging to two different units are aligned along the $c$ axis (figure 1), this interatomic distance variation reflects the inversion of the $c/a$ ratio.

All the Ni atoms are surrounded by 12 atoms with different A:Ni ratios ranging from 6:6 for Ni$_3$ atoms in the [AB$_2$] unit to 3:9 for Ni$_1$ and Ni$_4$ atoms in the [AB$_1$] unit. In La$_2$Ni$_7$, most of the Ni–Ni interatomic distances are between 2.45 and 2.62 Å, but significantly larger ones are obtained between Ni$_1$ and Ni$_4$ atoms with $d_{Ni-Ni} = 2.92$ Å. Upon Y for La substitution, most of the Ni–Ni interatomic distances are decreasing except the $d_{Ni$_1$-Ni$_3$}$ and $d_{Ni$_1$-Ni$_4$}$, which are slightly increasing.

The DFT calculated $a$, $c$, V/Z parameters and $c/a$ ratio have been added in figure 2 (star symbols). Individual $a$ and $c$ parameters follow a variation comparable to the experimental ones with a small deviation according to the GGA approximation which overestimates Y-richer parameters. However, resultant values as the evolution of the relaxed cell volume and $c/a$ ratio are both in rather good agreement with the experimental
Table 2. Chemical composition obtained from EPMA and cell parameters obtained from Rietveld refinement of the La$_{2-x}$Y$_x$Ni$_7$ compounds.

| $x$  | EPMA          | Hexagonal-2$H$ | Rhombohedral-3$R$ |
|------|---------------|---------------|-------------------|
| 0    | La$_2$Ni$_{86}$ | $a$ (Å) 5.067(1) $c$ (Å) 24.714(7) $V$ (Å$^3$) 548.57(2) wt% 100 | $a$ (Å) 5.0067(5) $c$ (Å) 36.483(4) $V$ (Å$^3$) 792.0(1) wt% 67 |
| 0.25 | Y$_{0.25}$La$_{1.77}$Ni$_{68.80}$ | 5.054(1) 24.630(1) 544.81(1) | 5.0067(5) 36.483(4) 792.0(1) |
| 0.5  | Y$_{0.5}$La$_{1.55}$Ni$_{69.94}$ | 5.040(2) 24.509(1) 539.26(4) | 5.0067(5) 36.483(4) 792.0(1) |
| 1    | Y$_{1.01}$La$_{0.99}$Ni$_{68.86}$ | 5.016(3) 24.359(2) 530.81(6) | 5.0067(5) 36.483(4) 792.0(1) |
| 1.2  | Y$_{1.18}$La$_{0.82}$Ni$_{67.01}$ | 5.0062(1) 24.324(5) 527.90(2) | 5.0067(5) 36.483(4) 792.0(1) |
| 1.4  | Y$_{1.39}$La$_{0.61}$Ni$_{68.91}$ | 4.9937(4) 24.273(2) 524.20(8) 27 | 5.0067(5) 36.483(4) 792.0(1) |
| 2    | Y$_2$Ni$_{6.92}$ | 4.9380(2) 36.189(2) 764.22(4) 100 | 5.0067(5) 36.483(4) 792.0(1) |

The $a$, $c$, $c/a$ and $V/Z$ cell parameters variations as well as the preferential Y site occupation among the two Wyckoff A sites calculated by DFT are in very good agreement with the experimental data. The anisotropic and inverse $c/a$ variation versus Y content can be explained by the interfacial constraints between the two $[AB_5]$ and $[AB_2]$ units. For $x < 1$, the $[AB_5]$ units contain only La atoms and the cell parameter variation upon Y substitution is mainly conducted by the $[AB_2]$ contraction. As the interface between the $[AB_5]$ and $[AB_2]$ units is in the basal plane, the contraction of the $[AB_2]$ units is limited in this direction to preserve the matching between the two types of units: the atom relaxation is therefore easier in the $c$ direction for the $[AB_2]$ units which are sandwiched between two $[AB_5]$ units. When Y substitutes La in the $[AB_2]$ unit, the cell parameters can relax in both $a$ and $c$ directions and the contraction in the basal plane becomes much easier to preserve the interface between the two units. Such anisotropic $c/a$ variation has already been observed in La$_5$Ni$_{19}$ and Pr$_5$Ni$_{19}$ compounds upon Mg for La and Pr substitution [48, 49]. The Mg atoms replace the La (or Pr) atoms located in the $[AB_2]$ units and the lattice contraction is much larger along the $c$ axis than along the $a$ axis. In Pr$_{3.75}$Mg$_{1.25}$Ni$_{19}$, the $c$ cell parameter contraction ($-1.5\%$) is twice as high as for the parameter $a$ ($-0.6\%$) [49].

The enthalpy of formation of the La$_{2-x}$Y$_x$Ni$_7$ compounds has been calculated considering the Y for La substitution in both possible interstitial sites ($[AB_5]$ and $[AB_2]$ units) using the rhombohedral description (figure 4). Comparable results are expected for both polymorphic structures, as shown in [41]. In fact, no clear $\Delta H_{\text{free}}$ difference between both symmetries is observed for the binaries La$_5$Ni$_7$ and Y$_5$Ni$_7$. For $x < 1$, the position of Y in the 6$c_2$ sites ($[AB_2]$ unit) leads
to a more stable structure until this site is fully occupied by Y. Then for larger substitution rates of Y, a progressive filling of the 6c1 site ([AB3] unit) is observed. The Y atoms show therefore a preferential occupation in the less coordinated site (CN16) compared to the one with larger coordination number (CN20). This preferential occupation in CN16 site is attributed to the smaller atomic radius of Y atoms compared to the La ones. This CN16 site contains more A neighbors and less Ni neighbors, in agreement with the experimental observations as discussed above.

3.2. Magnetic properties

The thermomagnetic curves $M(T)$ measured under an applied field of 0.1 T are plotted in figure 5. A distinct behavior is observed for $x < 1$ and $x \geq 1$. To see more clearly the evolution for $x < 1$, the corresponding curves are presented separately with appropriate scales. All the isothermal magnetization curves recorded at 5 K are compared in figure 6. The magnetic ordering temperatures and magnetic moments are reported in table 4. The influence of the few impurities observed by XRD on the intrinsic magnetic properties is discussed in the supplementary materials.

The magnetic curves of La$_2$Ni$_7$ agree with those of previous works showing an antiferromagnetic behavior and a metamagnetic transition toward a wFM state [14, 17, 34]. At 5 K, the critical field $H_{c1}$ obtained from the maximum curve derivative $dM/dH$ is equal to 4.6 T and the ferromagnetic state is reached at 6.5 T, these values are similar to those measured by Parker et al. at 4.2 K [12]. The small spontaneous magnetization $M_{spont} = 0.095 \mu_B$/f.u. at 5 K (0.048 $\mu_B$ at 300 K) can be attributed to a small quantity of ferromagnetic Ni particles (<0.1%), such impurities were not present in the $M(T)$ curves in references [12, 17] but observed in reference [13]. The saturation magnetization extrapolated at high field and corrected from the ferromagnetic Ni impurity is equal to 0.61 $\mu_B$/f.u. or 0.088 $\mu_B$/Ni atom. The thermal evolution of the transition fields, obtained from the derivative of the $M(\mu_0H)$ curves, is presented in figure 7 and will be discussed later. The $M(T)$ curves have been measured under different applied fields from 0.05 to 7 T (supplementary, figures S2(a) and S2(b)): a close examination shows that below 1 T the AFM broad peak displays three maxima, as it was observed but not detailed in previous works [12, 14, 15, 17]. Two maxima are still visible between 1 and 3 T and only a broad peak between 3 and 5.5 T. The temperature maxima denoted $T_{N1}$, $T_{N2}$ and $T_{N3}$ decrease versus applied field and show thermal hysteresis of 2–4 K between heating and cooling (supplementary, figures 6).

![Figure 4](image-url)
S2(c) and S2(d)). The relative peak intensity also changes versus temperature: the intensity of peaks 1 and 2 progressively decreases at the expense of the peak 3 which remains visible up to 5.5 T. The $f_{\text{peak2}}/f_{\text{peak3}}$ ratio decrease versus applied field is shown in inset of figure S2(c).

A tentative $\mu_0 H = f(T)$ phase diagram was proposed by Tazuke et al [17] using the isothermal $M(\mu_0 H)$ curves measured at different temperatures. They have assumed the existence of one AFM phase below transition fields $\mu_0 H_{c1}$ ($T \leq 37$ K) and $\mu_0 H_{c2}$ ($37$ K $\leq T < 54$ K) and two intermediate phases IM$_1$ ($T \leq 37$ K) and IM$_2$ ($37$ K $< T < 66$ K) below the third transition field $\mu_0 H_{c3}$, above which a FM behavior is found. It can be noticed that the three temperature maxima $T_{\text{Nn}}$ ($n = 1$ to 3) measured upon heating are located at 38 K, 52.2 K and 65 K respectively for an applied field of 0.05 T, and are close to the temperature boundaries observed by Tazuke et al [17].

This reveals a complex magnetic behavior of La$_2$Ni$_7$ which origin has still to be solved. The co-existence of different AFM ordering temperatures can be due for example to a complex helimagnetic structure with propagation vectors along the different crystallographic axis as it has been observed for holmium-based compounds [50–52].

For $x = 0.25$ and 0.5, a single AFM peak is observed for an applied field of 0.1 T with maxima at 57 K and 65 K respectively (figure 5). Contrary to La$_2$Ni$_7$, no splitting of the AFM peak can be observed on the thermomagnetic curves recorded in various applied magnetic fields. As the applied field increases, $T_N$ is shifted to lower temperature and disappears at 14 T for $x = 0.25$, whereas AFM peak with a maximum at 48 K is still observed at 14 T for $x = 0.5$ (figures 8(a) and 9(a)).

The magnetization isotherms $M_f(\mu_0 H)$ of both compounds display metamagnetic behaviors for $T < T_N$ (figures 8(b) and 9(b)). All the magnetization curves cross zero, indicating the absence of ferromagnetic impurities. The derivatives of the $M_f(\mu_0 H)$ curves reveal two transition fields $\mu_0 H_{c1}$ and $\mu_0 H_{c2}$ (supplementary: as example see figure S3). $\mu_0 H_{c1}$ saturates at about 2.5 T at 5 K for both substituted compounds. For La$_{1.75}$Y$_{0.25}$Ni$_7$, $\mu_0 H_{c2}$ increases continuously as $T$ decreases reaching 12.5 T at 5 K. This later metamagnetic transition shows a weak hysteresis below 20 K. For La$_{1.5}$Y$_{0.5}$Ni$_7$, the second transition field $\mu_0 H_{c2}$ could only be measured for 45 K $< T < 60$ K as below 45 K, the transition fields are larger than 14 T. The evolution of the transition fields versus temperature for $x = 0$, 0.25 and 0.5 has been plotted in figure 7.

The first transition field $\mu_0 H_{c1}$ around 2 T is barely sensitive to the temperature and the Y content. The second transition field $\mu_0 H_{c2}$ strongly varies versus temperature and Y content. $\mu_0 H_{c2}(T)$ increases versus temperature, and a scaling factor can be established: it is 2.65 time larger for $x = 0.25$ than for La$_2$Ni$_7$ and 6 time larger for $x = 0.5$. By extrapolation, $\mu_0 H_{c2}$ should reach about 28 T at 5 K for $x = 0.5$. In addition, for $x = 0.25$, we observe that $T_N = f(\mu_0 H)$ is equivalent to $\mu_0 H_{c2} = f(T)$.

The increase of $T_N$ and $\mu_0 H_{c2}$ confirms the stabilization of the AFM state compared to the FM state as the Y content increases. The first transition, between two AFM structures can be related to a spin-flop transition with a partial spin reorientation of the Ni moments upon applying magnetic field, whereas the second transition toward a FM state can be attributed to a spin-flip, with all Ni moments aligned parallel to the applied field. Such behavior has been proposed to describe the $\mu_0 H = f(T)$ phase diagram of metamagnetic compounds [53]. In this study, the existence of two metamagnetic transitions, a first order spin-flop transition with a constant transition field and a second spin-flip transition with a critical field decreasing with the temperature, has been attributed to centrosymmetric system with a weak anisotropy. The similarity of the proposed $\mu_0 H = f(T)$ phase diagram shape (see figure 4 of reference [53]) with our experimental results strongly suggest that hexagonal La$_{2-x}$Y$_x$Ni$_7$ compounds ($x < 1$), which crystallize in a centrosymmetric structure, are weak itinerant antiferromagnets with a weak anisotropy.
Table 4. Magnetic parameters of the La$_{2-x}$Y$_x$Ni$_7$ compounds.

| $x$ | $T_N$ (K) | $T_C$ (K) | $\mu_S$ at 5 K ($\mu_B$/f.u.) | $\theta$ (K) | $\mu_{\text{eff}}$ ($\mu_B$/Ni) | $q_C$ ($\mu_B$/Ni) | $q_C/q_S$ |
|-----|-----------|-----------|-----------------------------|-------------|-------------------------------|-----------------|---------|
| 0   | 50(2)     | 57(2)     | 0.61(1)$^b$                 | 0.088(1)    | 67$^c$                        | 0.80$^c$        | 0.28    | 3.2    |
| 0.25| 65(2)     | 57(2)     | 0.69(5)                    | 0.099(1)    | 60                           | 0.82            | 0.30    | 3.1    |
| 0.5 | 65(2)     | 57(2)     | 0.61(1)                    | 0.088(1)    | 60                           | 0.82            | 0.30    | 3.1    |
| 1   | 65(2)$^a$ | 53(2)     | 0.61(1)                    | 0.088(1)    | 60                           | 0.82            | 0.30    | 3.1    |
| 1.2 | 53(2)     | 53(2)     | 0.46(1)                    | 0.066(1)    | 52(2)                        | 0.88            | 0.33    | 3.3    |
| 1.4 | 54(2)     | 53(2)     | 0.51(8)                    | 0.074(1)    | 50(2)                        | 0.94            | 0.39    | 5.3    |
| 2   | 53(2)     | 53(2)     | 0.562(9)                   | 0.080(1)    | 50(2)                        | 0.90            | 0.38    | 4.8    |

$^a$For $\mu_0H > 3$ T;
$^b$Measured at $\mu_0H > 7$ T;
$^c$From reference [17].

This metamagnetic behavior can be attributed to itinerant electron metamagnetic transition associated to large spin fluctuations with competition between antiferromagnetic and ferromagnetic states.

The nature of the magnetic transitions can be estimated using the relation between the applied field and magnetization $M$, which is derived from the Landau development of the free energy at equilibrium:

$$\mu_0H = a_1(T)M + a_2(T)M^3 + a_3(T)M^5$$

where $a_1$, $a_2$ and $a_3$ are the Landau coefficients.

The first Landau coefficient $a_1$ corresponds to the inverse of the magnetic susceptibility, and is positive and maximum at $T_c$ or $T_N$. The sign of the second coefficient $a_2$ at the transition temperature indicates the nature of the transition: it is positive or equal to zero for a second order transition and negative for a first order transition at the transition temperature. The sign of the $a_3$ coefficient can be easily determined by plotting the Arrott–Belov curves:

$$M^2 = f(H/M)$$

The Arrott–Belov plots for $x = 0.25$ and 0.5 show below $T_N$, two S-shape behavior corresponding to the two metamagnetic transitions (figures 8(c) and 9(c) and zooms in figures S4 and S5). They both display negative slopes around $\mu_0H_{c1}$ and $\mu_0H_{c2}$ showing the first order character of these transitions. The change from positive to negative slope is clearly observed between 60 and 55 K for $x = 0.25$ and 65 and 60 K for $x = 0.5$, confirming the slight increase of $T_N$ versus Y concentration.

LaYNi$_7$ displays a very weak ferromagnetic behavior at low magnetic field, and an AFM behavior as the applied field increases (figure S6). LaYNi$_7$ has a single hexagonal structure, but Y atoms are substituted to La atoms on both A sites. This induces some kind of chemical disorder, which can favor a weak ferromagnetic contribution. It is also possible that some traces of rhombohedral phase exist, in too weak percentage to be detected by XRD, but enough to contribute to the magnetization at low field. Nevertheless, as the AFM peak is increasing upon applied field, it confirms that the main magnetic contribution is the AFM one. No metamagnetic transition field can be observed, even for the $M(\mu_0H)$ curves close to 60 K, indicating that the transition fields are larger than 9 T.

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All the $M(T)$ curves of compounds with $x > 1$ present a wFM behavior with $T_C$ around 53 K (figure 5(a)). The magnetization isotherms $M_T(\mu_0H)$ are characteristic of a ferromagnetic behavior (supplementary material, figure S7). The incomplete saturation of the $M_{12K}(\mu_0H)$ curve has been already observed for Y$_2$Ni$_7$ and attributed to the itinerant character of the ferromagnetism [22]. The main difference for the three compounds is the difference of extrapolated saturation magnetization ($\mu_S$) which increases with the Y content (figure 6).

The results obtained for rhombohedral Y$_2$Ni$_7$ agree well with previous works [22, 36, 54]. The smaller $\mu_S$ values observed for $x = 1.2$ and 1.4 can be attributed to the magnetic contribution of the hexagonal phase (33 and 27 wt%, respectively) which has a smaller magnetization than the rhombohedral one.

In all investigated compounds, the paramagnetic Curie temperatures $\theta$ are positive, which is a characteristic of ferromagnets as well as metamagnets, and the effective Ni moments $\mu_{\text{eff}}$ vary between 0.8 and 1 $\mu_B$/Ni. For $x = 1.4$, $\mu_{\text{eff}} = 0.94 \mu_B$/Ni, whereas the saturation moment measured at 5 K is $\mu_S = 0.074 \mu_B$/Ni. These values allow to calculate the Rhodes–Wohlfarth ratio (RWR = $q_C/q_S$ ($\mu^2_{\text{eff}} = q_C (q_C + 2)$; $\mu_S = q_S$)) which characterizes the itinerancy of the ferromagnetic state [22, 55].
canceled on the Ni5 site which is surrounded by 6 Ni1 atoms. The ordered moment in the AFM structure is low. The molecular field is large enough to induce a Ni moment on the Ni5 site and reverse the orientation of the Ni1 moments from antiparallel to parallel alignment. The DFT calculations suggest that a spin-flop transition with a change of Ni moment orientation but maintaining an AFM order is induced upon applied field. Unfortunately, neutron powder diffraction (NPD) experiments will not be helpful to solve these two AFM structures as the Ni moments are two small, and their contribution to the NPD pattern negligible. The increase of \(T_N\) and of the relative transition fields \(\mu_B H_c\) suggest that the AFM1 phase is stabilized upon Y substitution. As for the \(x = 0.25\) and \(x = 0.5\), the Y atoms are substituted only in the site belonging to the \([\text{AB}_1]\) unit, they should mainly influence the moments of the Ni5 and Ni1 neighboring atoms, by a charge transfer and a small modification of the DOS at \(E_F\). The AFM structure being characterized by the absence of ordered moment on the Ni5 site, its stabilization can originate from a larger charge transfer from the A element (A = La and Y) toward the Ni5 atom as explained in [35].

Considering the rhombohedral structure, the formation of a similar AFM structure will require at least a doubling of the magnetic cell along the \(c\) axis, as an even number of stacking of one \([\text{AB}_1]\) unit and two \([\text{AB}_2]\) units is necessary to obtain an equal number of antiparallel FM Ni layers. This would yield a very large anisotropic magnetic cell with \(c/a = 14.7\). In addition, the presence of stacking faults in such compounds, which contain a mixture of hexagonal and rhombohedral phases cannot fulfill the periodicity required for the wAFM structure.

All the compounds with \(x > 1\), containing a majority of rhombohedral phase, are wFM with the same Curie temperature \(T_C = 53\) K, determined by the maximum of the \(dM/d(\mu_B H)\) curves at 0.1 T. It might be surprising that \(T_C\) is not affected by the Y for La substitution. However, it should be considered that the magnetic properties arise from the Ni–Ni interactions, which contribute to the sharp and narrow peak in the DOS at \(E_F\). In those weak ferromagnets, the magnetic properties were estimated by extrapolation of the high magnetic measurements. The large values of RWR confirm the itinerant magnetic character of all these compounds and the values determined for \(x = 0.25\) and \(x = 0.5\) agree with previous works [17, 22]. In addition, all these compounds present large ordering temperatures (50–60 K) compared to small Ni moments (0.07–0.1 \(\mu_B\)) as expected for weak itinerant magnets.

The previous experimental results show that the \(x = 0.25\) compounds crystallize in a single hexagonal structure with \(x = 0\) and \(x = 1\) are weak antiferromagnets with metamagnetic behavior (metamagnets), whereas the one containing a rhombohedral phase with \(x > 1\) are weak ferromagnets. LaYNi5, which is just at the boundary, contains similar AFM structure will require at least a doubling of the magnetic cell along the \(c\) axis. As an even number of stacking faults in such compounds, which contain a mixture of hexagonal and rhombohedral phases cannot fulfill the periodicity required for the wAFM structure.
energy is proportional to the energy difference between the ferromagnetic state (SP state) and the paramagnetic state (NSP state). In reference [35], the calculated energy difference ($\Delta E = E_{\text{SP}} - E_{\text{NSP}}$) is very close for $3R - \La_2Ni_7$ (4.43 meV/Ni atom) and $3R - \Y_2Ni_7$ (5 meV/Ni atom), which corresponds to $T_c = 51$ and 58 K, respectively. This can explain that $T_c$ is not sensitive to the Y for La substitution in the rhombohedral structure for these weak itinerant magnets. The main difference between compounds with $x = 1.2, 1.4$ and 2 is related to the saturation magnetization, which increases with the Y content. Assuming that the ferromagnetic behavior is related to the rhombohedral phase as observed for $Y_2Ni_{17-x}$ compounds [20], the magnetization curves should be a mixture of ferromagnetic and antiferromagnetic phases. However, as the AFM magnetization is much smaller than the FM one, it contributes only to a decrease of the saturation magnetization.

Sensitivity of the magnetic order to the chemical composition has been observed upon Al, Co or Cu for Ni substitution in $Y_2Ni_7$. The Curie temperature decreases to zero with 1.5 at% of Al and 20 at% of Co [38] or 10 at% of Cu [58]. The collapse of ferromagnetism has been interpreted by a shift of $E_F$ toward the sharp slope of the DOS peak and consequently a fast decrease of the $N(E_F)$ due to these small Ni substitutions.

The influence of applied pressure on the evolution of the magnetic properties of these $A_2Ni_7$ compounds could be interesting not only to separate chemical and cell volume influence on their magnetic structures but also to check the possibility to reach a quantum critical point. For example, application of an external pressure on weak itinerant ferromagnet ZrZn2 leads to the observation of a quantum critical point at 2.35 GPa [59].

4. Conclusion

In the present study, both structural and magnetic properties of the $La_2-Y_2Ni_7$ system have been investigated. This system is very sensitive to the Y content and two different behaviors are clearly observed for $x \leq 1$ and $x > 1$. For $x \leq 1$, the stable structure is hexagonal, and the Y atoms replace preferentially the La atoms in the $[AB_2]$ units of lower coordination number (CN16). This leads to a reduction of the $c/a$ ratio because of geometric constraints between $[AB_2]$ and $[AB_3]$ units. For compounds with $1 < x < 2$, Y atoms occupy both $[AB_2]$ and $[AB_3]$ units and the compounds crystallize in a mixture of hexagonal and rhombohedral structures with an increase of the $c/a$ ratio. $Y_2Ni_7$ is purely rhombohedral.

The magnetic ground state changes from antiferromagnetic state for compounds with hexagonal structure and $x < 1$ to ferromagnetic state for compounds containing a rhombohedral phase with $x > 1$. $La_2Ni_7$ exhibits a complex magnetic phase diagram as its $M(T)$ curves display three AFM peaks, whose positions and relative intensities vary upon applying field. For $x = 0.25$ and 0.5, at least two itinerant metamagnetic transitions have been observed below $T_N$: a first one between two AFM structures and the second one corresponding to an AFM–FM transition. The critical field $\mu_0H_{c2}$ corresponding to an AFM–FM transition increases with the substituted Y content, indicating a stabilization of the AFM phase. This result also confirms that the AFM structure is stabilized for $A_2Ni_7$ compounds crystallizing in the hexagonal structure and with Y substituted only in the $[AB_2]$ unit. $2H - LaYNi_7$ compound has mainly an antiferromagnetic behavior but shows some weak ferromagnetic contribution, at low field, which can be related to the substitution of Y on both $[AB_2]$ and $[AB_3]$ sites.

The rhombohedral compounds with $x > 1$ are all weak ferromagnets with $T_c$ close to 53 K. The Curie temperature remains constant versus Y content indicating very similar magnetic Ni–Ni exchange interaction and only small variations of the saturation magnetization are observed.

These results highlight the correlation of the magnetic properties with the structural changes induced by the Y for La substitution in $La_2Ni_7$. Further works will be undertaken to determine the influence of the La substitution by a magnetic rare earth on both structural and magnetic properties of these compounds.

Acknowledgments

We are thankful to M Warde for her participation in the synthesis of some compounds presented in this work. We also thank E Leroy for the EPMA analysis and F Maccari for the magnetic measurements of $La_1.5Y_{0.5}Ni_7$ up to 14 T at TU Darmstadt (Germany). DFT calculations were performed using HPC resources from GENCI-CINES (Grant 2019-96175).

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