The nano-microfibrous $R_{11}Ni_4In_9$ intermetallics: new compounds and extraordinary anisotropy in $Tb_{11}Ni_4In_9$ and $Dy_{11}Ni_4In_9$

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Abstract

$R_{11}Ni_4In_9$ (R = rare earth) compounds exhibit an unusual self-assembled nano/microfibrous morphology that results in anisotropic structural and magnetic behaviors. The existence of new compounds for R = Dy, Ho, Er, Tm and Lu, has been established (orthorhombic $Nd_{11}Pd_4In_9$ -type, $oC48$, $Cmmm$, $Z = 2$), showing that the formation of these phases, previously known for R = La-Nd, Sm, Gd-Tb and Y, extends to all of the rare earth elements, except Sc, Eu and Yb. The results of physical property measurements performed on oriented fibers of $Tb_{11}Ni_4In_9$, $Dy_{11}Ni_4In_9$ and $Y_{11}Ni_4In_9$ are presented. Multiple magnetic transitions are observed in $Tb_{11}Ni_4In_9$ and $Dy_{11}Ni_4In_9$ with the highest ordering temperature, T_C , of 112 and 88 K, respectively. $Y_{11}Ni_4In_9$ is a Pauli paramagnet down to 2 K. The fibrous microstructure of these compounds leads to a strong anisotropy in their electrical resistivity and magnetization behaviors. The c -axis of the orthorhombic cell is the easy magnetization and high electrical-conductivity direction. Ferrimagnetic-like behavior, with extremely high coercive fields ($H_C = 6.6$ T for $Tb_{11}Ni_4In_9$ at 5 K and $H_C = 5.7$ T for $Dy_{11}Ni_4In_9$ at 2 K), is found when the fibers (and the c -axis) are oriented parallel to the magnetic field direction; antiferromagnetic-like ground state is observed with the fibers oriented orthogonal (*i.e.*, in the a - b plane). Appearance of a Griffiths phase regime is observed in both compounds before entering the ordered magnetic states. This is more evident for fibers orthogonal to the magnetic field and is even preserved at 1 T. Field induced spin-flop magnetic transitions are also observed in $Tb_{11}Ni_4In_9$ and $Dy_{11}Ni_4In_9$ with fibers orthogonal and parallel to the field, respectively.

First principles calculations have been performed for several representative compounds to explain the underlying phase stability and their magnetism.

Keywords: Rare earth intermetallics; Nanowires; Magnetic shape anisotropy; Fiber compounds; Ferrimagnetic ordering.

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1. Introduction

$\text{Gd}_{11}\text{Ni}_4\text{In}_9$ and other $\text{R}_{11}\text{Ni}_4\text{In}_9$ (R = rare earth) compounds show an interesting and unusual morphology: they form as a bundle of fibers, directly crystallized as the alloy solidifies from the melt [1,2]. The $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds are the first example of an intermetallic phase forming a distinctly fibrous morphology directly from the melt without any additional treatment or processing. The fibers grow along the temperature gradient established by melting and crystallization technique; their size is of the order of $1\mu\text{m}$ in cross section, with length ranging from ≈ 1 to tens of mm. The most important factor leading to the peculiar microfibrillar morphology in the $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds is the presence of short (and strong) In–In bonds in the a - b plane which creates strongly bonded $[\text{R}_8\text{Ni}_4\text{In}_9]_\infty$ columns growing along the c -axis.

The formation of $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds was previously reported for La-Nd, Sm, Gd, Tb, and Y [3]. They belong to the family of compounds with the general formula $\text{R}_{m+n}\text{M}_{2n}\text{X}_m$ ($m = 9$, $n = 2$) and are isostructural with the $\text{Nd}_{11}\text{Pd}_4\text{In}_9$ -type ($oC48$, $Cmmm$, $Z = 2$) [4]. The crystal structure of these compounds is formed by AlB_2 (RNi_2) and CsCl (RIn)-type fragments; it is layered, with layers of R alternating with layers of Ni/In atoms. The unit cell has long a and b axes (14-15 Å and 21-22 Å, respectively) and a short c axis (≈ 3.6 Å). We have checked the existence of new compounds in the $\text{R}_{11}\text{Ni}_4\text{In}_9$ family [5,6] and found that this phase also forms for all the trivalent heavy lanthanides Dy, Ho, Er, Tm and Lu. No $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds are formed with Sc and divalent Eu and Yb. We have ascertained that all of the $\text{R}_{11}\text{Ni}_4\text{In}_9$ phases, including $\text{Y}_{11}\text{Ni}_4\text{In}_9$, as well as the newly found $\text{R}_{11}\text{Pd}_4\text{In}_9$ and $\text{R}_{11}\text{Pt}_4\text{In}_9$ compounds, have the microfibrillar structure [2]. Besides the $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds (45.83 at.% R, 16.67 at.% Ni, and 37.50 at.% In), an additional phase, from the $\text{R}_{m+n}\text{M}_{2n}\text{X}_m$ family is formed in the R-Ni-In ternary systems at a very close composition: the $\text{R}_5\text{Ni}_2\text{In}_4$ phase ($m = 4$, $n = 1$) (45.45 : 18.18 : 36.36 at.%, respectively), that crystallizes in the orthorhombic $\text{Lu}_5\text{Ni}_2\text{In}_4$ -type structure [7] ($oP22$, $Pbam$, $Z = 2$). The $\text{R}_5\text{Ni}_2\text{In}_4$ alloys, as well as $\text{Gd}_5\text{Pt}_2\text{In}_4$ [8] and the newly identified $\text{Gd}_5\text{Pd}_2\text{In}_4$ phase [2], do not show evidence of fibers; they have a normal approximately equiaxed metallic microstructure. The presence of impurity RNiIn and $\text{R}_5\text{Ni}_2\text{In}_4$ phases in the alloys of the 11:4:9 composition likely prevented the discovery of both the 11:4:9 compounds for most of the heavy R [3,9,10], and their fibrous morphology.

To date, anisotropic physical properties have been investigated only for the $\text{Gd}_{11}\text{Ni}_4\text{In}_9$ compound using naturally formed oriented fibers [1,2]. The particular fibrous microstructure is responsible for the strong anisotropy in the chemical, physical and mechanical properties found in this compound, which shows uniaxial anisotropy and easy magnetization direction along the rapid growth direction, which is parallel to the c -axis. Here we report on the physical properties (magnetic susceptibility, isothermal magnetization, heat capacity and electrical resistivity) of the

Tb₁₁Ni₄In₉, Dy₁₁Ni₄In₉ and Y₁₁Ni₄In₉ phases. The strong anisotropy due to the peculiar fibrous microstructure of these three phases is quite evident in the physical properties. A complex magnetic ordering occurs in these compounds, due to five crystallographically inequivalent sites occupied by rare earth atoms which give rise to different magnetic sublattices. At low temperature, in the Tb and Dy compounds the magnetic interactions among the five R sublattices give rise to a predominant ferrimagnetism along the *c*-axis and to antiferromagnetism in the *a*-*b* plane. Interesting spin-flop magnetic transitions, induced by the applied magnetic field, are observed in Tb₁₁Ni₄In₉ with the fibers orthogonal to the field and in Dy₁₁Ni₄In₉ with the fibers parallel. Moreover, the establishment of a Griffiths phase regime is also observed in both compounds in the paramagnetic region before they undergo long-range magnetic orderings; these short-range magnetic states appear to be preserved in magnetic field of 1 T.

A neutron diffraction investigation of some of these R₁₁Ni₄In₉ compounds (namely R = Tb and Ho) is now underway to investigate their magnetic structures and to better understand the magnetic ordering and properties. While this work was in progress, reports on the magnetic properties of Dy₁₁Ni₄In₉ [9] and R₁₁Ni₄In₉ (R = Pr, Nd, Sm, Gd and Tb) [10] appeared in the literature. Though our results are in overall agreement with those reported, we studied the unexpectedly unusual anisotropic behavior of these compounds which was not addressed in the earlier papers. First principles calculations have been performed for some representative compounds of this series to explain both the underlying structural stability in comparison with R₅Ni₂In₄ compounds and their magnetic states.

2. Experimental procedures

Samples (6-8 g) were prepared by arc melting, under an inert Ar atmosphere using high purity metals: 99.9+ wt.% (99.8 at.%) purity with respect to all other elements in the periodic table R metals were obtained from the Materials Preparation Center of the Ames Laboratory [11]; 99.99 wt.% Ni and 99.999 wt.% In were purchased from commercial vendors. The elements were weighed in stoichiometric proportions. The buttons were remelted at least four times, turning them upside-down each time for better homogenization. Weight losses were between 0.2-0.5 %. The samples were wrapped in a Ta foil, sealed under vacuum in quartz ampoules, and annealed at 1000°C for 7-14 days. The alloys were single phase, except those formed by Er, Tm and Lu, which contained small amounts of the 5:2:4 phase: from ~ 3 vol.% for the Er alloy to ~ 6 vol.% for the Lu alloy.

Lattice parameters were calculated by the least square method after indexing the X-ray Guinier powder patterns [Cu K α_1 radiation; Si as internal standard, $a = 5.4308(1)$ Å]. X-ray powder diffraction patterns for Rietveld refinement were collected on a PANalytical X'Pert Pro

diffractometer (monochromated Cu $K\alpha_1$ radiation). Filings of the $R_{11}\text{Ni}_4\text{In}_9$ samples (due to their high ductility, see next section) were prepared, sealed in a pyrex tube under vacuum, and annealed at 400 or 500°C for 3-7 days, in order to relieve stress and obtain good powder patterns.

Heat capacity data were collected using an automated semi-adiabatic calorimeter from 2 to 300 K and in magnetic fields from 0 to 2 T [12]. The DC magnetization was measured as a function of both temperature (in the range 2-350 K) and applied magnetic fields [0 to 7 T using a Magnetic Property Measurement System (MPMS, Quantum Design) or 0 to 14 T using a Physical Property Measurement System (PPMS, Quantum Design)]. Resistivity measurements were recorded using a four-probe automated setup between 2 and 300 K and in zero field.

3. Results and discussion

3.1. Crystal structure of the $R_{11}\text{Ni}_4\text{In}_9$ phases

The research concerning the formation of homologous phases in $R_{11}\text{Ni}_4\text{In}_9$ intermetallics allowed us to identify the following new compounds: $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, $\text{Ho}_{11}\text{Ni}_4\text{In}_9$, $\text{Er}_{11}\text{Ni}_4\text{In}_9$, $\text{Tm}_{11}\text{Ni}_4\text{In}_9$ and $\text{Lu}_{11}\text{Ni}_4\text{In}_9$. Preliminary results have already been presented in Refs. [2,5,6]. The present investigation enabled us to confirm the $R_{11}\text{Ni}_4\text{In}_9$ compounds to exist for the following rare earth elements Y, La-Nd, Sm, Gd-Tm, and Lu. Structurally, these compounds are quite interesting. They are built from well-defined columns (or rods) due to presence of short In-In chemical bonds [In1–In1 (site 8q) and In2–In2 (site 8q)] on the a - b plane quickly growing along the short c -axis (Fig. 1a). The rods have " $R_8\text{Ni}_4\text{In}_9$ " stoichiometry (Fig. 1b) and their rapid growth generates the peculiar nano/microfibrous morphology of these compounds with long microwires (several mm) forming bundles (Fig. 2).

The crystallographic data obtained by X-ray powder diffraction, including lattice parameters (a , b , c), unit cell volume (V_{obs}), and volume contraction (ΔV %) {where the volume contraction is defined as $\Delta V \% = [(V_{\text{calc}} - V_{\text{obs}})/V_{\text{calc}}] \times 100$, with V_{calc} being the calculated unit cell volume obtained as a sum of the atomic volumes [13]} of the $R_{11}\text{Ni}_4\text{In}_9$ compounds are listed in Table 1. The Rietveld refinement plots of the $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ compounds are shown in Fig. 3 (Fig. 3a and 3b for Tb and Dy phases, respectively), while the refinement data and the atomic coordinates are listed in Table 2. The Rietveld refinements have been performed by using the FULLPROF software [14]. The preparation of the homologous ' $\text{Sc}_{11}\text{Ni}_4\text{In}_9$ ' compound was attempted but the sample contained $\text{Sc}_5\text{Ni}_2\text{In}_4$ as a nearly single-phase material. The formation of the corresponding Eu and Yb compounds was also probed, but neither the 11:4:9 nor the 5:2:4 phases were observed.

Fig. 4 shows a plot of the lattice parameters *versus* the rare-earth R^{3+} ionic radius for the $R_{11}\text{Ni}_4\text{In}_9$ series. It is seen that the lattice parameters increase linearly from Lu to La, including Y,

following the well-known *lanthanide contraction* trend. An analogous linear trend is found for the unit cell volume (V_{obs}), as seen in Fig. 5a; the data point for $\text{Ce}_{11}\text{Ni}_4\text{In}_9$, which lies on the straight line established by the other lanthanides, indicates Ce is trivalent in this compound. Trend of the volume contraction ΔV % *versus* the rare earth R^{3+} ionic radius is shown in Fig. 5b. The ΔV values decrease from the heavy R to the light ones; two different trends, possessing two slightly different slopes, are apparently followed by the heavy and the light lanthanides, respectively. The compounds with larger volume of formation values are expected to be more stable, and therefore, the most stable phases are the ones formed by Y and the heavy lanthanides. However, the existence of the $\text{R}_5\text{Ni}_2\text{In}_4$ phases (formed by the heavy R and Sc) enters in competition with the formation of the $\text{R}_{11}\text{Ni}_4\text{In}_9$ phases. La and Y have higher values that lie well above the general trends established by the other R elements. Therefore, and based on the above assumption, the thermodynamic stability of the $\text{R}_{11}\text{Ni}_4\text{In}_9$ phases increases from La to Lu.

3.2. Physical properties of $\text{Tb}_{11}\text{Ni}_4\text{In}_9$, $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ and $\text{Y}_{11}\text{Ni}_4\text{In}_9$

3.2.1. Heat capacity

The heat capacity of $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ has been measured between 2-300 K in zero and applied magnetic fields (1 and 2 T for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$; 0.5, 1 and 2 T for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$). In Fig. 6 the data are shown for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$, between 80-150 K (Fig. 6a) and 18-40 K (Fig. 6b). The heat capacity of $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ shows three anomalies: a major peak at 112 K (Fig. 6a) followed by a weaker peak at 31 K and a minor anomaly at 23 K. Below 4 K, the heat capacity shows an upturn attaining a substantial value of about 1 J/mol K near 1.8 K (inset of Fig. 6b), which is due to the high temperature tail of the Tb nuclear Schottky anomaly. The heat capacity data for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ are shown in the temperature ranges between 60-120 K in Fig. 7a and 2-16 K in Fig. 7b. $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ has just two peaks: a major one at 87 K (Fig. 7a) followed by a weaker and a broad anomaly at 10 K (Fig. 7b). In both compounds, the high-temperature peak broadens and shifts toward higher temperatures in an applied magnetic field; these results suggest that both $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ order either ferro- or ferrimagnetically (FM or FIM) at 112 K and 87 K, respectively. Further, in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ the peak at 31 K clearly moves to lower temperatures without noticeable broadening under applied magnetic field, indicating a spin reorientation to an antiferromagnetic (AFM) state (Fig. 6b), while the minor anomaly at about 23 K is not affected significantly by the magnetic field (Fig. 6b). The broad peak in $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ observed around 10 K remains nearly unaffected by applied magnetic field (Fig. 7b).

Fig. 8 shows the heat capacity of $\text{Y}_{11}\text{Ni}_4\text{In}_9$ between 2 and 350 K. Unlike the Dy and Tb analogs, the heat capacity of $\text{Y}_{11}\text{Ni}_4\text{In}_9$ does not show any anomalies over the entire range as expected for a paramagnetic compound. Although the chemical behavior of Y is very similar to that

of the lanthanides and its atomic size very close to that of Dy, unlike the magnetic rare earths it does not possess 4f electrons and it is therefore non-magnetic. We fitted the heat capacity data to the following expression over the entire temperature range [15]:

$$C = \gamma T + m C_{Debye} + (1-m) C_{Einstein}$$

The first term, where γ is the electronic specific heat constant, represents the electronic contribution to the heat capacity, the remaining two terms are the phonon contribution which includes both the Debye and Einstein terms, C_{Debye} and $C_{Einstein}$, respectively. The expressions for C_{Debye} and $C_{Einstein}$ are:

$$C_{Debye} = 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad \text{with } x = \theta_D/T$$

$$C_{Einstein} = 3R \frac{y^2 e^y}{(e^y - 1)^2} \quad \text{with } y = \theta_E/T$$

where θ_D and θ_E are the Debye and Einstein temperatures, respectively, R is the gas constant and T the temperature [15]. The fit parameters are: $\gamma = 57$ mJ/mol K² (2.37 mJ/gram atom/K²), $\theta_D = 206.5$ K, $\theta_E = 356.5$ K and $m = 0.83$. Since the optical frequency (Einstein temperature) is larger than that of Debye, we assign the Ni atoms in the unit cell to Einstein mode and the remaining atoms to the Debye modes. Such an assignment is in accordance with the relative fractions of (R+In) : Ni atoms as 20 : 4 = 5 : 1. With $m = 0.83$, the ratio $m : (1-m)$ is close to 5:1. Here we assume that Ni, being the lightest atom in the unit cell, can vibrate at a relatively higher frequency.

3.2.2. Electrical resistivity

The zero-field electrical resistivity data of Tb₁₁Ni₄In₉, Dy₁₁Ni₄In₉ and Y₁₁Ni₄In₉ between 2 and 300 K are shown in Figs. 9a, 9b and 9c, respectively. The measurements have been carried out on oriented fibers parallel and orthogonal to the electrical current direction. Clear anomalies are evident at about 110 K and 30 K for the Tb compound and at about 90 K and 10 K for Dy₁₁Ni₄In₉, especially with current orthogonal to the fibers. The resistivity data are in a good agreement with, and corroborate, the results from heat capacity. A strong anisotropy is seen in the electrical resistivity of these compounds, with the resistivity at room temperature 2-3 times higher in Tb and Dy compounds, and up to about 10 times higher in Y₁₁Ni₄In₉, when the fibers are oriented orthogonal to the current.

Similar to the Tb and Dy compounds, the resistivity in $\text{Y}_{11}\text{Ni}_4\text{In}_9$ decreases with decreasing temperature; however, no anomalies are seen over the whole temperature range as expected for a simple Pauli paramagnet (see below). The resistivity of $\text{Y}_{11}\text{Ni}_4\text{In}_9$ varies by an order of magnitude for the two directions at 2 K: $10\ \mu\Omega\text{cm}$ when the fibers are parallel and $141\ \mu\Omega\text{cm}$ when the fibers are orthogonal, while the corresponding values at 300 K are 47 and $435\ \mu\Omega\text{cm}$.

3.2.3. Magnetic properties

The magnetic susceptibility of $\text{Y}_{11}\text{Ni}_4\text{In}_9$ is nearly temperature independent with a value of about $1.06 \times 10^{-5}\ \text{emu/g}$ (data not shown). The weak Pauli paramagnetic behavior of $\text{Y}_{11}\text{Ni}_4\text{In}_9$ shows that the Ni 3d band is filled and Ni is non-magnetic in these compounds, in agreement with what was observed in Refs. [2] and [10].

The magnetic susceptibility, M/H , of $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ was measured between 2 and 350 K and in magnetic fields of 0.1 and 1 T, with applied field parallel and orthogonal to the fibers direction, respectively. The data between 0 and 250 K are shown in Figs. 10a and 10b for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and 10c and 10d for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$. The magnetic transitions have been probed by measuring the magnetization in the zero-field-cooled (ZFC) and field-cooled (FC) modes. In $\text{Tb}_{11}\text{Ni}_4\text{In}_9$, both the ZFC and FC magnetization data at 0.1 T show a rapid upturn near 120 K followed by thermomagnetic irreversibility at lower temperatures (Fig. 10a), in addition to significant anisotropy between the two directions. Transition temperatures of $T_C = 111\ \text{K}$ and $T_{N1} = 31\ \text{K}$ were obtained from peaks in the first derivative of the M vs. T data, with an additional anomaly at 23 K; they were identical for both fibers parallel and orthogonal to the magnetic field. They correspond to the peaks in the heat capacity around the same temperatures. On the other hand, the ZFC and FC magnetization data at 1 T coincide down to nearly 30 K; at lower temperatures, weak thermomagnetic irreversibility is present, but the anisotropy between the two directions remains (Fig. 10b). The rapid upturn near 120 K is due to the ferro/ferrimagnetic ordering of the Tb ions, but from our data we cannot infer whether all or only a few of the five distinct sublattices of Tb ions are ordering magnetically. The drop in the ZFC magnetization below 50 K (0.1 T) is most likely due to large coercivity of this material at low temperature, as the ZFC plot (1 T) is qualitatively different. Of course, the peak in the 30-40 K range in both the ZFC and FC plots (0.1 and 1 T) is due to the antiferromagnetic transition already identified in the heat capacity measurement. Similar arguments apply in the case of $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ as well, with an evident and strong anisotropy between the two orientations of the fibers with respect to the magnetic field vector (Figs. 10c and Fig. 10d). Here again, the shape of the magnetization curves below 100 K is determined by an interplay of the applied magnetic field, exchange interactions and coercivity; the magnetization data show a rapid upturn below 100 K. From the peak in the first derivative of M vs. T , a $T_C = 88\ \text{K}$

is obtained for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, both for fibers parallel and orthogonal to the magnetic field; this temperature is in a good agreement with the corresponding peak in the heat capacity observed at 87 K. The data also show an anomaly at about 10 K, which is related to the second magnetic transition distinctly seen as a relatively broad peak in the heat capacity data.

For both compounds, the inverse magnetic susceptibility, $1/\chi = H/M$, at high temperatures and in the paramagnetic region varies linearly with the temperature following the Curie-Weiss law [$\chi = C_{\text{CW}}/(T - \theta_p)$] (see Fig. 11); the 0.1 and 1 T data practically coincide, indicating the absence of ferromagnetic impurities. A least-squares fit of the data for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ (above 225 and 170 K for the fibers parallel and orthogonal, respectively) yields an effective magnetic moment $\mu_{\text{eff.}} = 9.7 \mu_B/\text{f.u.}$ and a paramagnetic Curie temperature $\theta_p = 56.2$ K with fibers parallel, and $\mu_{\text{eff.}} = 9.9 \mu_B/\text{f.u.}$ and $\theta_p = 18.5$ K with fibers orthogonal to the magnetic field, respectively (Figs. 11a and 11b). The corresponding values for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ (for linear fits above 170 and 105 K for the fiber parallel and orthogonal, respectively) are $\mu_{\text{eff.}} = 10.8 \mu_B/\text{f.u.}$ and $\theta_p = 37.4$ K, and $\mu_{\text{eff.}} = 11.0 \mu_B/\text{f.u.}$ and $\theta_p = -12.8$ K for fibers parallel and orthogonal to the magnetic field, respectively (Figs. 11c and 11d). The values of the effective magnetic moments are close to the theoretical values of $9.72 \mu_B$ and $10.65 \mu_B$ for the free Tb^{3+} and Dy^{3+} ions, respectively [16]. On the other hand, the values of θ_p are markedly different for the field applied along the two directions, and in the Dy compound θ_p even changes sign between the two directions. Such planar-*versus*-axial anisotropic magnetic properties become even more evident from the isothermal magnetization measurements (that will be discussed below). The magnetic susceptibility data are thus in agreement with the fibrous nature of these compounds, since in a polycrystalline material with random orientations of the crystallites θ_p should be constant. Positive θ_p indicates *prima-facie* a predominant ferromagnetic exchange interaction; however, it may be noted that in Dy compound, despite the negative value of θ_p for fibers orthogonal to the field, the positive θ_p for fibers parallel to H is positive and larger.

In the paramagnetic region, the inverse magnetic susceptibility shows in both compounds, and for both the fibers parallel or orthogonal to the magnetic field vector, a clear downturn well above T_C (Figs. 11a-d). This feature, similar to that observed in $\text{Tb}_5\text{Si}_2\text{Ge}_2$ [17], suggests the development of a Griffiths phase, characterized by short range ferromagnetic clustering [18,19], which could be due to competing interactions among the five different Tb(Dy) sublattices. Interestingly, the downward curvature, which is more evident for fibers orthogonal to the magnetic field vector (Figs. 11b and 11d), is preserved even in a relatively high magnetic field of 1 T.

Because of the five rare earth sublattices, the overall magnetic ordering is likely complex as it depends upon the strengths and signs of intra and inter-sublattice exchange interactions. Heat capacity data presented above already indicate the presence of both ferromagnetic (or ferrimagnetic)

and antiferromagnetic transitions in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$. A neutron diffraction work is now underway; the results will help to shed light on the magnetic orderings and structures of these compounds.

Isothermal magnetization has been measured with field parallel and perpendicular to fibers at 5, 25 and 50 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ (Figs. 12a and 12b), at 2, 20 and 40 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ (Figs. 13a and 13b) and up to 14 T. The comparison between the data shows an extraordinarily different response depending on the direction of the field with respect to the fibers, confirming the strong magnetocrystalline anisotropy of these materials. Overall, for both Tb and Dy compounds the measurements show a ferro/ferrimagnetic behavior for the fibers parallel to the magnetic field and an antiferromagnetic behavior with fibers orthogonal. Similar to $\text{Gd}_{11}\text{Ni}_4\text{In}_9$ [2], the magnetization of these two isostructural compounds does not saturate even at the highest applied magnetic field of 14 T.

The isothermal magnetization measured at 50 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ (up to 7 T) and at 40 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ (up to 14 T) with fibers oriented parallel to the field (Fig. 12a and 13a) shows a qualitatively similar behavior: when cooled down from room temperature, the magnetically ordered phase reveals a narrow hysteresis with magnetization that quickly reaches high values even at low fields but does not saturate. This behavior suggests a ferrimagnetic structure associated with the magnetic transitions at the highest temperature. At lower temperatures (25 and 5 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$; 20 and 2 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$), a substantial difference is observed in the isothermal magnetization whether the fibers are oriented parallel (Figs. 12a and 13a) or orthogonal (Figs. 12b and 13b) to the magnetic field. In $\text{Tb}_{11}\text{Ni}_4\text{In}_9$, with the fibers parallel to H, the hysteresis loops become broader as the temperature is reduced first to 25 K and then further down to 5 K. Weak metamagnetic signatures observed at $T = 5$ K in the demagnetization curves around 4 T are consistent with the antiferromagnetic re-ordering observed below 31 K in the zero-field heat capacity. Very large coercive fields, H_C , of 1.1 and 6.6 T are obtained at 25 and 5 K, respectively, in this compound (Fig. 12a). An apparently similar magnetic behavior is observed in $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ with fibers parallel to H (Fig. 13a). Broad hysteresis loops, with high coercive fields of 2.0 and 5.7 T, are obtained at 20 and 2 K, respectively. The extremely high coercive fields at low temperatures are likely related to a strong shape anisotropy that arises due to a distinctly fibrous microstructure. Such extraordinarily high H_C values are comparable to those found in the $\text{R}_2\text{Fe}_{14}\text{B}$ compounds [20], even though in the present case this unconventional coercivity has a different nature due to shape anisotropy.

Interestingly, the hysteresis loops of $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ with fiber parallel to the magnetic field show a spin-flop transition at high fields between 10 and 14 T (Fig. 13a). The spin-flop transition, which at 2 K is hysteretic, becomes fully reversible at 20 K but still remains visible even at 40 K. Following the Néel's terminology, the term "spin-flop" was originally used to define a field induced reorientation of the magnetic moments present in easy-axis antiferromagnets driven by the external

magnetic field [21]. However, since then, similar mechanisms, as well other different field-driven reorientation effects (where the spins on two sublattices flip from antiparallel to parallel at a high field), have been found in strong-anisotropy antiferromagnetic systems and nanostructured materials [22]. The presence of the spin-flop transition in the $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ with fibers oriented parallel to the field is a strong evidence of a ferri to ferromagnetic reordering (or perhaps to another ferrimagnetic configuration with a larger total moment) along the c -axis, or of a transition from an antiferromagnetic sublattice to a ferri-ferromagnetic state. Neutron scattering measurements at high magnetic fields would be required to determine the magnetic structures. A similar behavior has been observed in single crystal CaCo_2As_2 along the c -axis of its tetragonal cell [23]. For $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, the isothermal magnetization at 2 K has also been recorded on the same specimen after having tilted the fibers by 10° and 30° with respect to the parallel orientation to the field (Fig. 14). By increasing the tilting angle the large coercivity value remains the same, but the spin-flop transition flattens (the hysteresis remains the same of ≈ 3 T) and eventually disappears when the fibers are orthogonal to the field (Fig. 13b). This behavior confirms the prominent shape-anisotropy effects in these materials.

A different and complicated behavior is found when the fibers are orthogonal to H (Figs. 12b and 13b). The isothermal magnetization measured at 50 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ (inset of Fig. 12b) and 40 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ (Fig. 13b) shows narrow hysteresis loops and a trend characteristic of a ferrimagnetic material. The magnetization recorded at lower temperatures, *i.e.* 25 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ (Fig. 12b) and 20 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ (Fig. 13b), highlights for both compounds a magnetic behavior similar to each other, narrow hysteresis, low remanence values and loops which remain open until high magnetic fields are reached. These trends are indicative of a strong antiferromagnetic components present at these temperatures in both compounds when the fibers are orthogonal to the magnetic field. At the lowest temperature of 5 K and 2 K (for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, respectively), in both compounds the hysteresis loop is definitely narrower in the Tb compound and almost closed in Dy compound. At this temperature, $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ shows an interesting hysteresis loop with several metamagnetic transitions (Fig. 12b); here again, a spin-flop transition is observed at low field, which is similar to that reported for TbNiAl_4 [24]. On the other hand, $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ has a weak metamagnetism with a nearly reversible hysteresis loop (Fig. 13b), likely associated with the AFM transition below 11 K, as seen in heat capacity and $M(T)$ data.

The magnetization measurements performed up to 14 T and at 5 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and 2 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ allowed an estimate of the saturation moment for the R atom: saturation moments of 5.8 and $6.3 \mu_B/\text{Tb}$ and 8.4 and $5.2 \mu_B/\text{Dy}$ have been obtained for the fibers oriented parallel and orthogonal to the magnetic field vector, respectively. The theoretical effective saturation moment is $9 \mu_B$ per Tb atom and $10 \mu_B$ per Dy atom if all R moments are aligned parallel. The fact that these

values are significantly lower than the theoretical moment is in agreement with a ferrimagnetic ground state in the $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ compound. An analogous magnetic behavior was already observed in the $\text{Gd}_{11}\text{Ni}_4\text{In}_9$ compound [2]. In the case of Tb, Dy and other non-*S* rare earth ions, crystalline electric fields can also result in a lower saturation magnetization than that expected on the basis of free-ion behavior.

3.3. Theoretical calculations

Local spin density approximation (LSDA), including onsite electron correlations (Hubbard *U*) LSDA+*U* [25], calculations have been performed for the $\text{Gd}_5\text{Ni}_2\text{In}_4$, $\text{Tb}_5\text{Ni}_2\text{In}_4$, $\text{Gd}_{11}\text{Ni}_4\text{In}_9$, and $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ compounds within tight-binding linear muffin tin orbital [26] and full potential linear augmented plane wave band structure methods [27]. LSDA calculations have been performed for $\text{Y}_5\text{Ni}_2\text{In}_4$ and $\text{Y}_{11}\text{Ni}_4\text{In}_9$ compounds assuming no onsite electron-electron correlations. The *k*-space integrations have been performed with $32 \times 32 \times 32$ Brillouin zone mesh for the convergence of total charge and total energy. Since the *4f* states exhibit strong onsite correlations in the R atoms of the $\text{Gd}_5\text{Ni}_2\text{In}_4$, $\text{Tb}_5\text{Ni}_2\text{In}_4$, $\text{Gd}_{11}\text{Ni}_4\text{In}_9$ and $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ compounds, the LSDA+*U* with model *U* = 6.7 eV and *J* = 0.7 eV parameters corrects the positioning of occupied and unoccupied *4f* states by shifting occupied *4f* states below the Fermi level and unoccupied *4f* states above the Fermi level. In these calculations, the crystallographic data of the $\text{Nd}_{11}\text{Pd}_4\text{In}_9$ -type $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds reported here and in Ref. [2], and those of the $\text{Lu}_5\text{Ni}_2\text{In}_4$ -type $\text{R}_5\text{Ni}_2\text{In}_4$ compounds given in Ref. [6] have been used. As pointed out in a recent paper [6], the formation energy, calculated by subtracting the total energy of the constituents from the total energy of the compound, is lower by 442, 337, and 163 meV/cell in $\text{Tb}_5\text{Ni}_2\text{In}_4$, $\text{Dy}_5\text{Ni}_2\text{In}_4$, and $\text{Y}_5\text{Ni}_2\text{In}_4$, respectively, compared to the hypothetical “ $\text{Gd}_5\text{Ni}_2\text{In}_4$ ” which does not form. Hence, $\text{Tb}_5\text{Ni}_2\text{In}_4$, $\text{Dy}_5\text{Ni}_2\text{In}_4$, and $\text{Y}_5\text{Ni}_2\text{In}_4$ ($\text{Lu}_5\text{Ni}_2\text{In}_4$ -type) are more stable than “ $\text{Gd}_5\text{Ni}_2\text{In}_4$ ”. On the other hand, the formation energies of $\text{Y}_{11}\text{Ni}_4\text{In}_9$, $\text{Gd}_{11}\text{Ni}_4\text{In}_9$, and $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ are −15.642, −18.830, and −19.306 eV/cell, respectively; this indicates that the compound stability is enhanced in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ compared to $\text{Gd}_{11}\text{Ni}_4\text{In}_9$.

The ferromagnetic total energy in $\text{Gd}_{11}\text{Ni}_4\text{In}_9$ is lower by 95.287 meV/cell compared to the ferrimagnetic total energy, indicating the ferromagnetic ground state in this compound. Here the ferrimagnetic configuration has been modeled by assigning Gd1, Gd3, and Gd5 in the spin up and Gd2 and Gd4 in the spin down directions. The total energy calculations with other possible spin up/down configurations between different Gd atoms also showed higher total energy in the ferromagnetic configuration indicating the ferromagnetic ground state. This theoretical result contradicts the experimental observation of Ref. [2], which indicated ferrimagnetic ground state. On the other hand, it suggests that a simple collinear magnetic structure is unstable, and a more

complex non collinear state may be present. It is noted that the non-collinear spin-polarized calculations in such a large unit cell with a large number of Gd atoms are not feasible at present.

In order to differentiate the magnetic behavior of $R_{11}Ni_4In_9$ from that of structurally closely related $R_5Ni_2In_4$ compounds, we have analyzed magnetic moments and density of states of these compounds. The atom projected spin magnetic moments from spin polarized ferromagnetic calculations for “ $Gd_5Ni_2In_4$ ” and $Tb_5Ni_2In_4$ are shown in Table 3. The $4f$ spin moments of Gd and Tb atoms in $R_5Ni_2In_4$ are $7 \mu_B/Gd$ and $6 \mu_B/Tb$. Due to structural anisotropy, spin polarized $5d$ moments of three non-equivalent R atoms are different. The exchange splitting (splitting between spin up and spin down conduction electron states) is higher in “ $Gd_5Ni_2In_4$ ” compared to $Tb_5Ni_2In_4$ (Fig. 15, Table 3), leading to slightly higher conduction-electron magnetic moments in “ $Gd_5Ni_2In_4$ ”. The moments on Ni and In atoms are negligible in both compounds.

The atom projected spin magnetic moments from spin polarized ferromagnetic calculations for $Gd_{11}Ni_4In_9$ and $Tb_{11}Ni_4In_9$ are shown in Table 4. Similar to $R_5Ni_2In_4$, the $4f$ spin moments of Gd and Tb atoms are $7 \mu_B/Gd$ and $6 \mu_B/Tb$, and due to the structural anisotropy, the spin polarized $5d$ moments of the non-equivalent 5 R atoms are also different. Induced Ni and most of the In magnetic moments are negligible, but notably, the spin polarized magnetic moments of In3 are non-negligible in both the Gd and Tb compounds. Hence, strong Gd (Tb) $5d$ and In3 $5p$ hybridization, due to the short In3–In3 chemical bonds, may play a role in the stability of the $[R_8Ni_4In_9]_\infty$ structural rods. Furthermore, the DOS curves around the Fermi level of paramagnetic $Y_5Ni_2In_4$ and $Y_{11}Ni_4In_9$ compounds (Fig. 16) are different. The Fermi level falls at a peak of the DOS in $Y_5Ni_2In_4$ while it is located slightly away in $Y_{11}Ni_4In_9$ (towards the valley), thereby indicating potentially higher stability of $Y_{11}Ni_4In_9$ compared to that of $Y_5Ni_2In_4$ in agreement with total energy results.

4. Conclusions

We report on the existence of new members in the $R_{11}Ni_4In_9$ family of fibrous compounds, *i.e.* the compounds with $R = Dy, Ho, Er, Tm$ and Lu . Neither Eu and Yb form the $R_{11}Ni_4In_9$ nor the $R_5Ni_2In_4$ phase; this is due to the divalent character of these two lanthanides in the metallic 11:4:9 and 5:2:4 indides. However, Sc forms only the 5:2:4 phase. Some physical properties measured on oriented fibers of $Tb_{11}Ni_4In_9$, $Dy_{11}Ni_4In_9$ and $Y_{11}Ni_4In_9$ are reported. The unusual and peculiar property of the $R_{11}Ni_4In_9$ compounds to crystallize in self-assembled nano/microfibers, which translates into a macroscopic microwire morphology of the alloys, is responsible for the strong anisotropy in the physical properties obtained. The c -axis of the orthorhombic cell is the easy magnetization and high electrical-conductivity direction. Ferrimagnetic behavior, with extremely high coercive fields H_C of 6.6 T for $Tb_{11}Ni_4In_9$ (at 5 K) and of 5.7 T for $Dy_{11}Ni_4In_9$ (at 2 K) is found when fibers are oriented parallel to the magnetic field direction; antiferromagnetic ground state is

instead observed when the fibers are oriented orthogonal (on the a - b plane). Heat capacity and magnetization measurements together suggest that there are three magnetic ordering phenomena occurring in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ involving the five distinct lanthanide sublattices at low temperature. A plausible explanation of the magnetic behavior found in the two compounds is that ferromagnetic-like transitions, that occur at high temperature (112 K and 88 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, respectively), are followed by antiferromagnetic rearrangements at low temperatures (below 31 K and 10 K for $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ and $\text{Dy}_{11}\text{Ni}_4\text{In}_9$, respectively). A net downturn curvature in the inverse magnetic susceptibility is shown by both compounds (for either the fibers parallel or orthogonal to the field) in the paramagnetic region before entering the ordered magnetic states. This feature suggests the formation of an intermediate regime typical of a Griffiths phase, characterized by short range ferromagnetic clustering, due to competing interactions among the five different R sublattices. This feature, more evident for fibers orthogonal to the magnetic field vector, is preserved even at a high magnetic field of 1 T. At lower temperatures, the spin-flop transitions induced by the magnetic field are observed in the hysteresis loops in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ for fibers orthogonal to the field and in $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ with fibers parallel. Such spin-flop re-orderings are evidence of transitions from antiferromagnetic (or ferrimagnetic) to ferri-ferromagnetic states.

Analysis of the formation energy at 0 K indicates $\text{Tb}_5\text{Ni}_2\text{In}_4$, $\text{Dy}_5\text{Ni}_2\text{In}_4$, and $\text{Y}_5\text{Ni}_2\text{In}_4$ are more stable than “ $\text{Gd}_5\text{Ni}_2\text{In}_4$ ”, while the compound stability is enhanced in $\text{Tb}_{11}\text{Ni}_4\text{In}_9$ compared to $\text{Gd}_{11}\text{Ni}_4\text{In}_9$. The strong R $5d$ and In $3p$ hybridization, due to the short In-In chemical bonds, may be responsible for creating the structural rods along the c -axis in $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds. The Fermi level, falling slightly away from the DOS peak, indicates higher stability of paramagnetic $\text{Y}_{11}\text{Ni}_4\text{In}_9$ compound compared to that of $\text{Y}_5\text{Ni}_2\text{In}_4$ phase in which the Fermi level falls at a DOS peak.

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Figures caption

Fig. 1. (In color on line) Skeletal projection along the a -axis (a), and perspective projection along the rods direction (b), of the crystal structure of the $R_{11}Ni_4In_9$ compounds.

Fig. 2. (In color on line) Scanning Electron Microscopy (SEM) images of a $Y_{11}Ni_4In_9$ specimen showing the microfibers at increasing magnification (fibers length ranging from few to tens of mm, and $\approx 1 \mu m$ in cross section); 100 μm scale (a), 30 μm scale (b), 10 μm scale (2, d), 3 μm scale (e, f).

Fig. 3. (In color on line) Rietveld refined X-ray diffraction patterns of the $Tb_{11}Ni_4In_9$ (a) and $Dy_{11}Ni_4In_9$ (b).

Fig. 4. (In color on line) Variations of the lattice parameters *vs.* the rare earth R^{3+} ionic radius for the $R_{11}Ni_4In_9$ compounds; the full symbols indicate the new compounds identified in this work.

Fig. 5. (In color on line) Trend of the unit cell volume V_{obs} , (a) and volume contraction $\Delta V \% = [(V_{calc} - V_{obs})/V_{calc}] \times 100$, (b) *vs.* the R^{3+} ionic radius for the $R_{11}Ni_4In_9$ compounds (the full symbols indicate the new compounds identified in this work).

Fig. 6. (In color on line) Heat capacity measurements, in zero and two applied magnetic fields, *vs.* temperature, for $Tb_{11}Ni_4In_9$ in the ranges 80-150 K (a), 18-40 K (b), and 1.8 to 8 K (b inset) respectively.

Fig. 7. (In color online) Heat capacity measurements, in zero and several applied magnetic fields, *vs.* temperature, for $Dy_{11}Ni_4In_9$ in the ranges 60-120 K (a) and 2-16 K (b), respectively.

Fig. 8. (In color on line) Heat capacity measurements in zero field *vs.* temperature, for $Y_{11}Ni_4In_9$ in the range 2-350 K. Solid line is the fit to the Debye-Einstein function.

Fig. 9. (In color on line) Electrical resistivity of $Tb_{11}Ni_4In_9$ (a), $Dy_{11}Ni_4In_9$ (b) and $Y_{11}Ni_4In_9$ (c) between 2 and 300 K (in zero magnetic field), measured orienting the fibers parallel and orthogonal to the electric current.

Fig. 10. (In color on line) DC magnetic susceptibility (M/H) *vs.* temperature measured on oriented fibers between 2 and 250 K for $Tb_{11}Ni_4In_9$ at 0.1 T (a) and 1 T (b) and for $Dy_{11}Ni_4In_9$ at 0.1 T (c) and 1 T (d).

Fig. 11. (In color on line) Plots of inverse susceptibility measured on oriented fibers between 2 and 350 K and at 0.1 T and 1 T for $Tb_{11}Ni_4In_9$ (a,b) and $Dy_{11}Ni_4In_9$ (c,d). The straight line is the fit to the Curie-Weiss law (from 0.1 T data). The insets show the data on larger scale.

Fig. 12. (In color on line) Isothermal magnetization of $Tb_{11}Ni_4In_9$ measured at 5, 25 and 50 K, on fibers parallel (a) and orthogonal (b) to the magnetic field vector.

Fig. 13. (In color on line) Isothermal magnetization of $Dy_{11}Ni_4In_9$ measured at 5, 20 and 40 K, on fibers parallel (a) and orthogonal (b) to the magnetic field vector.

Fig. 14. (In color on line) Isothermal magnetization at 2 K for $\text{Dy}_{11}\text{Ni}_4\text{In}_9$ recorded after tilting the fibers by 10° and 30° with respect to the magnetic field direction. The inset shows, on an enlarged scale, the field induced spin-flop transition appearing in between 10 and 14 T.

Fig. 15. (In color on line) The total density of states (DOS) of “ $\text{Gd}_5\text{Ni}_2\text{In}_4$ ” (a) and $\text{Tb}_5\text{Ni}_2\text{In}_4$ (b) compounds. The paramagnetic (PM) DOS of $\text{Tb}_5\text{Ni}_2\text{In}_4$ is not shown in (b) because the PM DOS is similar to that of the “ $\text{Gd}_5\text{Ni}_2\text{In}_4$ ”.

Fig. 16. (In color on line) The total density of states (DOS) in the paramagnetic $\text{Y}_5\text{Ni}_2\text{In}_4$ and $\text{Y}_{11}\text{Ni}_4\text{In}_9$ compounds.

Table 1.

Lattice parameters, observed unit cell volume (V_{obs}) and volume contraction (ΔV %) for all the $R_{11}\text{Ni}_4\text{In}_9$ compounds ($\text{Nd}_{11}\text{Pd}_4\text{In}_9$ -type, *oC48*, *Cmmm*, N° 65).

$R_{11}\text{Ni}_4\text{In}_9$	Lattice parameters			$V_{\text{obs}} [\text{\AA}^3]$	ΔV [%]	Ref.
	a [$\text{\AA}$]	b [$\text{\AA}$]	c [$\text{\AA}$]			
$\text{La}_{11}\text{Ni}_4\text{In}_9$	15.0061(4)	22.5039(7)	3.8347(2)	1295.0	6.3	*
	15.0173(9)	22.515(2)	3.8381(1)	1297.7	6.1	[3]
$\text{Ce}_{11}\text{Ni}_4\text{In}_9$	14.843(2)	22.203(3)	3.7760(8)	1244.4	6.0	*
	14.8506(7)	22.222(1)	3.7797(1)	1247.3	5.8	[3]
$\text{Pr}_{11}\text{Ni}_4\text{In}_9$	14.791(1)	22.164(2)	3.7542(1)	1230.7	6.7	[3]
$\text{Nd}_{11}\text{Ni}_4\text{In}_9$	14.726(3)	22.075(3)	3.731(1)	1213.0	7.4	*
	14.7288(8)	22.084(1)	3.7324(1)	1214.0	7.4	[3]
$\text{Sm}_{11}\text{Ni}_4\text{In}_9$	14.600(1)	21.903(2)	3.6880(2)	1179.4	8.5	[3]
$\text{Gd}_{11}\text{Ni}_4\text{In}_9$	14.4750(7)	21.742(2)	3.6549(4)	1150.2	10.6	*
	14.4802(6)	21.7597(9)	3.6575(1)	1152.4	10.4	[3]
$\text{Tb}_{11}\text{Ni}_4\text{In}_9$	14.398(1)	21.627(2)	3.6236(5)	1128.3	10.8	*
	14.4060(7)	21.639(1)	3.6284(1)	1131.1	10.6	[3]
$\text{Dy}_{11}\text{Ni}_4\text{In}_9$	14.347(2)	21.535(4)	3.607(2)	1114.4	11.0	*
$\text{Ho}_{11}\text{Ni}_4\text{In}_9$	14.2879(9)	21.468(2)	3.599(1)	1103.8	11.2	*
$\text{Er}_{11}\text{Ni}_4\text{In}_9$	14.236(2)	21.379(3)	3.583(1)	1090.5	11.5	*
$\text{Tm}_{11}\text{Ni}_4\text{In}_9$	14.1889(8)	21.317(2)	3.5671(6)	1078.9	11.6	*
$\text{Lu}_{11}\text{Ni}_4\text{In}_9$	14.107(1)	21.197(2)	3.5469(8)	1060.6	12.2	*
$\text{Y}_{11}\text{Ni}_4\text{In}_9$	14.366(2)	21.592(3)	3.6319(7)	1126.6	12.6	*
	14.327(4)	21.497(6)	3.6070(9)	1110.9	13.8	[3]

* this work

Table 2.

Rietveld refinement data obtained for Tb₁₁Ni₄In₉ and Dy₁₁Ni₄In₉ compounds (Nd₁₁Pd₄In₉-type, *oC48*, *Cmmm*, N° 65).

Atom	Wyckoff site	Atomic coordinates			Occupation
		x	y	z	
Tb₁₁Ni₄In₉ , $a = 14.408(1) \text{ \AA}$, $b = 21.642(1) \text{ \AA}$, $c = 3.6288(2) \text{ \AA}$					
Tb1	8 <i>p</i>	0.2476(2)	0.1703(1)	0	1
Tb2	4 <i>i</i>	0	0.1654(2)	0	1
Tb3	4 <i>i</i>	0	0.3767(1)	0	1
Tb4	4 <i>g</i>	0.3114(2)	0	0	1
Tb5	2 <i>a</i>	0	0	0	1
Ni	8 <i>q</i>	0.3510(3)	0.1034(3)	1/2	1
In1	8 <i>q</i>	0.1051(1)	0.2623(1)	1/2	1
In2	8 <i>q</i>	0.1505(1)	0.0728(1)	1/2	1
In3	2 <i>c</i>	1/2	0	1/2	1

R_B = 1.7 %, R_{wp} = 9.0 %, R_F = 2.2 %, χ^2 = 1.00 (GoF = 0.97)

Dy₁₁Ni₄In₉ , <i>a</i> = 14.344(1) Å, <i>b</i> = 21.554(2) Å, <i>c</i> = 3.6180(3) Å					
Dy1	8 <i>p</i>	0.2461(5)	0.1690(4)	0	1
Dy2	4 <i>i</i>	0	0.1607(4)	0	1
Dy3	4 <i>i</i>	0	0.3780(4)	0	1
Dy4	4 <i>g</i>	0.3120(6)	0	0	1
Dy5	2 <i>a</i>	0	0	0	1
Ni	8 <i>q</i>	0.348(1)	0.101(1)	1/2	1
In1	8 <i>q</i>	0.1047(4)	0.2626(4)	1/2	1
In2	8 <i>q</i>	0.1499(6)	0.0717(4)	1/2	1
In3	2 <i>c</i>	1/2	0	1/2	1

R_B = 1.1 %, R_{wp} = 7.2 %, R_F = 1.5 %, χ^2 = 0.96 (GoF = 0.95)

Table 3.

Calculated spin magnetic moments of non-equivalent atoms in “Gd₅Ni₂In₄” and Tb₅Ni₂In₄. The values in parenthesis are for Tb.

Atom	Wyckoff site	Magnetic moment [μ_B /atom]
Gd1 (Tb1)	<i>2a</i>	7.39 (6.32)
Gd2 (Tb2)	<i>4g</i>	7.23 (6.14)
Gd3 (Tb3)	<i>4g</i>	7.33 (6.24)
Ni	<i>4h</i>	−0.04 (0.00)
In1	<i>4h</i>	0.03 (0.02)
In2	<i>4h</i>	0.05 (0.02)

Table 4.

Calculated spin magnetic moments of non-equivalent atoms in Gd₁₁Ni₄In₉ and Tb₁₁Ni₄In₉. The values in parenthesis are for Tb.

Atom	Wyckoff site	Magnetic moment [μ_B /atom]
Gd1 (Tb1)	<i>8p</i>	7.32 (6.20)
Gd2 (Tb2)	<i>4i</i>	7.48 (6.31)
Gd3 (Tb3)	<i>4i</i>	7.19 (6.11)
Gd4 (Tb4)	<i>4g</i>	7.20 (6.11)
Gd5 (Tb5)	<i>2a</i>	7.32 (6.19)
Ni	<i>8q</i>	−0.04 (−0.02)
In1	<i>8q</i>	0.02 (0.00)
In2	<i>8q</i>	0.02 (0.01)
In3	<i>2c</i>	0.11 (0.06)

(a)

(b)

Graphical abstract