Magnetic properties of RY_2Ni_9 compounds and their hydrides $(R = La, Ce)$

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Abstract

The magnetic properties of the RY_2Ni_9 ternary alloys $(R = La, Ce)$ and their hydrides have been investigated. Both LaY_2Ni_9 and CeY_2Ni_9 are ferromagnets with $T_C = 15$ and 92 K, respectively. Upon H absorption $LaY_2Ni_9H_{12}$ becomes a Pauli paramagnet, whereas $CeY_2Ni_9H_8$ remains ferromagnetic with an additional magnetic contribution of trivalent Ce atoms belonging to the $MgZn_2$ units occupied by hydrogen atoms.
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1. Introduction

Recently, new interest has been devoted to the study of ternary RM_3-type compounds RM_2Ni_9 ($R = Y$, rare earth, Ca and $M = Mg$, Ca, Ti or Y) for hydrogen storage by solid-gas or electrochemical routes [1–6]. These compounds crystallize in an ordered variant of the $PuNi_3$-type rhombohedral structure which can be described as a stacking of $CaCu_5$ and $MgZn_2$ units [7]. The investigation of the crystallographic and hydriding properties of RY_2Ni_9 alloys has revealed two different behaviours for $R = La$ and Ce [6,8–10]. The crystal structure analysis of LaY_2Ni_9 has shown that this compound is isostructural to $LaMg_2Ni_9$ ($R\bar{3}m$ space group) with a preferential occupation of La atoms in the $3a$ site and of the Y atoms in the $6c$ sites [6]. It can absorb up to 13 H/f.u., with an isotropic expansion along the $\vec{a}$ and $\vec{c}$ axis. The hydrogen atoms are located in both $CaCu_5$ and $MgZn_2$ units [10]. CeY_2Ni_9 is isostructural to YNi_3 ($R\bar{3}m$ space group) with a statistical substitution of Y by Ce atoms in both $3a$ and $6c$ sites [6]. It absorbs only eight H atoms/f.u., which are located only in the $MgZn_2$ units [10]. A very anisotropic cell expansion was observed with a small contraction along the $\vec{a}$ axis (-2%) and a large

expansion along the $\vec{c}$ axis (27.6%). In addition, this leads to a volume expansion of 47% in the $MgZn_2$ units and a volume contraction of 2.6% in the $CaCu_5$ units. The very large cell volume expansion in the $MgZn_2$ units cannot be explained only by the H atom insertion and an additional volume increase related to a change of the Ce valence was expected. X-ray absorption (XAS) measurements at the Ce L_{III} edge indicated that the total Ce valence decreased from $v = 3.36$ to 3.17 upon H absorption [8]. This Ce valence is larger than that observed for a fully loaded compound like $CeNi_2H_4$ ($v = 3.03$) [11]. As the Ce_{3a} are located in the $CaCu_5$ units which are hydrogen free, it was assumed that their valence remained unchanged ($v = 3.36$). On the other hand the Ce_{6c} atoms, which are located in the hydrogen-filled $MgZn_2$ units, become nearly trivalent ($v = 3.05$). $CeY_2Ni_9H_8$ is the first-known Ce-based metallic hydride which is in a heterogeneous mixed valence state [8].

The aim of the present study was to investigate the magnetic properties of the ternary RY_2Ni_9 alloys and their hydrides. Hydrogen absorption is known to induce significant changes of the magnetic properties of inter-metallic compounds due to the variations of the cell volume and electronic properties. In addition, magnetic properties should be very sensitive to the change of Ce valence upon H absorption as observed in other metal hydrides compounds [12–16].

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2. Experimental

The RY_2Ni_9 alloys ($R =$ La, Ce) were prepared as described in [6]. The composition and the homogeneity of the alloys were checked by electron probe microanalysis and X-ray diffraction. The hydrides were prepared by solid-gas reaction using the Sievert method to determine the H content. Their cell parameters were checked by X-ray diffraction analysis. The X-ray diffractometer was a Bruker AXS D8, using the Cu$K\alpha$ radiation and equipped with a backscattered rear graphite monochromator.

The magnetic measurements were performed with a Physical Properties Measurement System (PPMS) from Quantum Design, working from 2 to 310 K and with a maximum applied field of 90 kOe.

3. Results and discussion

The cell parameters of the RY_2Ni_9 alloys and their hydrides were in good agreement with previous studies [6,9,10]. Magnetic measurements have been performed on LaY_2Ni_9 and CeY_2Ni_9 intermetallic compounds and their related hydrides $LaY_2Ni_9H_{12}$ and $CeY_2Ni_9H_8$. In Fig. 1 are reported the magnetization curves versus temperature and the applied field for LaY_2Ni_9. This compound orders ferromagnetically below a Curie temperature T_C of 15 K. The isothermal magnetization at 5 K had not reached saturation even at 90 KOe and the extrapolation at $H = 0$ leads to $M_S = 0.33(1)\,\mu_B$. The reverse susceptibility χ^{-1} follows a Curie–Weiss law with a paramagnetic temperature θ_p of 25 K. Since weak ferromagnetic impurities are observed in the paramagnetic range, probably due to the segregation of small Ni particles at the surface of the material [17], the Curie constant was determined using the slopes of the isotherm magnetization in the linear part of the high field region. This leads to a Curie constant of 0.29 emu/mol and an effective moment μ_{eff} of 1.53 μ_B. All the magnetic results are summarized in Table 1.

The isofield and isotherm magnetization curves of CeY_2Ni_9 are reported in Fig. 2. The value of T_C at 92 K is higher than for LaY_2Ni_9, and the saturation magnetization at 5 K is smaller: 0.23 μ_B. The reverse susceptibility is close to that of LaY_2Ni_9 above 150 K, but a significant deviation is observed below this temperature (Fig. 3). The extrapolation of χ^{-1} below 150 K leads to $\theta_p = 84$ K. The effective moment calculated with the slope of the $M(H)$ curves $\mu_{eff} = 1.46\,\mu_B$ is slightly smaller than for LaY_2Ni_9 (Table 1). This indicates that the Ce atoms remain nonmagnetic in CeY_2Ni_9, otherwise an increase of the effective moment should be observed. This result is in agreement with previous XAS measurements on CeY_2Ni_9 which have shown that the Ce atoms are in a valence fluctuating state ($v = 3.36$) [8].

The isofield and isotherm magnetizations of $LaY_2Ni_9H_{12}$ (Fig. 4) show a strong decrease compared to its parent intermetallic. The isotherm magnetizations display a weak ferromagnetic contribution which decreases slightly as the temperature increases up to 290 K. The spontaneous magnetization at 290 K (0.121 emu/g) is about 20 times larger than in LaY_2Ni_9 ($M_s = 0.007$ emu/g). This ferromagnetic contribution can be attributed to small Ni particles segregated at the surface upon hydrogen absorption as it has been observed in $LaNi_5$ after hydrogen cycling [18]. The evolution of the magnetization versus temperature is characteristic of an enhanced Pauli paramagnet and χ^{-1} does not follow a Curie–Weiss law (Fig. 3).
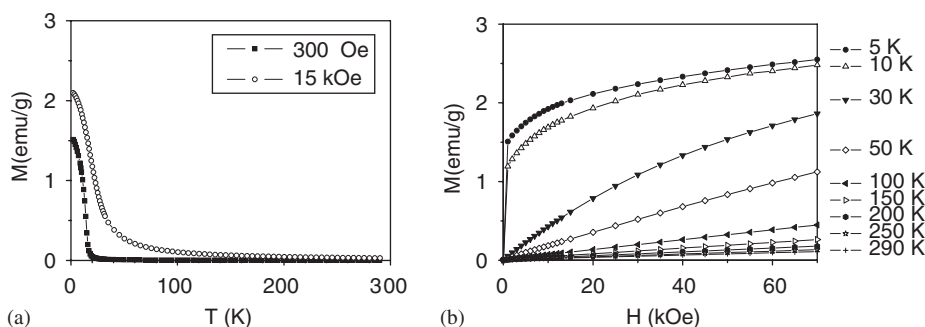

Fig. 1. Isofield (a) and isotherm (b) magnetizations of LaY_2Ni_9.

Table 1
Magnetic results for $RY_2Ni_9H_x$ compounds ($R =$ La, Ce)

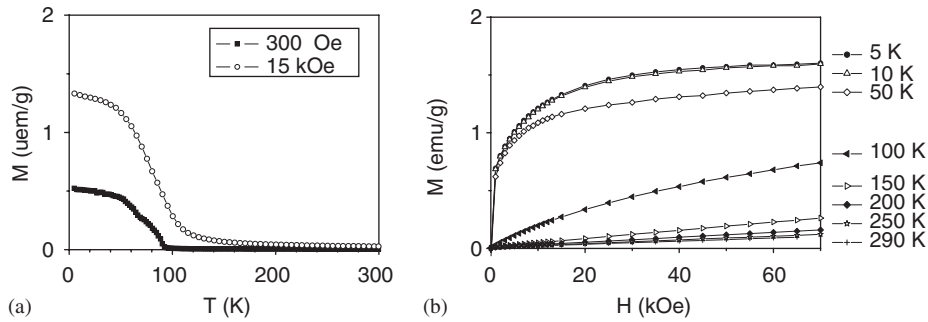| Compound	V (Å^3)	T_C (K)	M_s (μ_B) (5 K)	θ_p (K)	C (emu/mole)	μ_{eff} (μ_B)	χ (μ_B) $\times 10^6$ (290 K)
LaY_2Ni_9	538.3	15	0.33(1)	25	0.320(1)	1.60 (1)	0.222(1)
CeY_2Ni_9	524.6	92	0.23(1)	84	0.256(1)	1.43(1)	0.209(1)
$LaY_2Ni_9H_{12}$	672.3		0.056(1)				0.084(1)
$CeY_2Ni_9H_8$	629.5	77	0.47(1)	42	0.708(1)	2.38(1)	0.481(2)

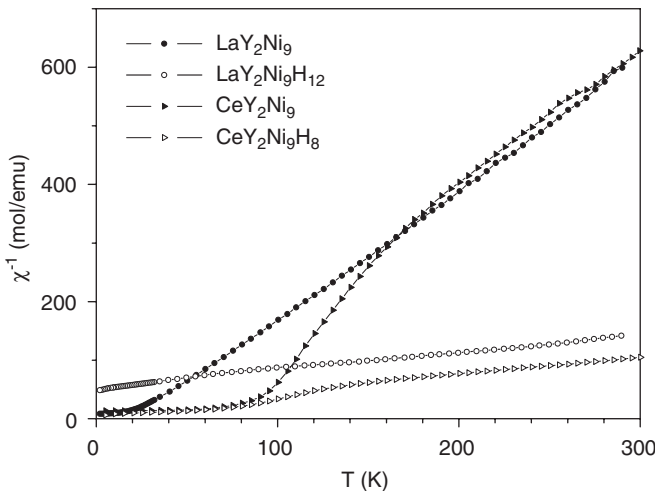Fig. 2. Isofield (a) and isotherm (b) magnetizations of CeY_2Ni_9.

Fig. 3. Reverse susceptibility of the RY_2Ni_9 alloys and their hydrides.

$CeY_2Ni_9H_8$ displays a ferromagnetic behaviour below $T_C = 78$ K (Fig. 5). Like for $LaY_2Ni_9H_{12}$, a larger ferromagnetic contribution than in the pristine compound is observed in the high-temperature range due to Ni segregation at the surface of the compound (Fig. 6). In addition, $CeY_2Ni_9H_8$ shows a sharp increase of the magnetization at low temperatures, which was not seen in the parent compound (Fig. 6). This additional contribution can be related to the contribution of magnetic trivalent Ce atoms. Previous XAS measurements have shown that the Ce valence has decreased from 3.36(1) in CeY_2Ni_9 to 3.17(1) in $CeY_2Ni_9H_8$. As reported in the introduction, this decrease is explained by the trivalent state of the Ce_{6c} belonging to the $MgZn_2$ units. The average composition in the $MgZn_2$ units is $Ce_{0.31}Y_{0.69}Ni_2$ and corresponds to $n_{6c} = 62\%$ ($n = $ at% of Ce). The percentage of Ce_{3a} is $n_{3a} = 38\%$ and the total Ce valence:

$$v_{CeY_2Ni_9H_8}$$
$$= n_{6c}v_{6c} + n_{3a}v_{3a} = 0.62 \times 3.05 + 0.38 \times 3.36 = 3.17.$$

The refinement of the reverse susceptibility of $CeY_2Ni_9H_8$ (using M/H slopes) leads to a Curie constant of 0.706 emu/mol and to $\mu_{eff} = 2.38 \mu_B$. This effective moment is close to the experimental Ce^{3+} effective moment which is $2.4 \mu_B$. However, the Ni magnetic contribution should be taken into account. Assuming that the Curie constant originating from the Ni atoms is the same than in CeY_2Ni_9 ($C = 0.265$ emu/mol) and that only 62% of the Ce atoms are trivalent ($C = 0.446$ emu/mol), then a total Curie constant of 0.711 emu/mol is obtained in very good agreement with the experimental value of 0.706 emu/mol. Therefore, both magnetic and XAS experiments confirm the assumption that the Ce_{6c}, which are located in the expanded $MgZn_2$ units, become trivalent and magnetic upon hydrogen absorption whereas the Ce_{3a} remain in a valence fluctuating and non-magnetic state. The change of Ce valence upon H absorption has been already observed in several Ce-based metal hydrides and was explained by a decrease of the hybridization between the Ce(4f) electrons and those of the conduction band [12–16,19]. Band structure calculations on CeNiIn and its hydride have shown a major influence of the volume expansion on the onset of the magnetization on cerium upon H absorption [20].

It is also valuable to compare the magnetic behaviour of these compounds with the magnetic properties of other RNi_3 phases ($R = $ Mg, Y, La and Ce) and their hydrides. This study has shown that both LaY_2Ni_9 and CeY_2Ni_9 are ferromagnetic below T_C. YNi_3 was considered as a very weak ferromagnet with $T_C = 33$ K and a saturation magnetization of $0.16 \mu_B$ [21–24], $CeNi_3$ is a Pauli paramagnet [24,25] and $LaNi_3$ an itinerant antiferromagnet with a metamagnetic behaviour [24,26,27]. Additionally, $LaMg_2Ni_9$ is a Pauli paramagnet and $CeMg_2Ni_9$ displays a Curie–Weiss behaviour with $\mu_{eff} = 3.61 \mu_B$ [28]. The magnetic properties of LaY_2Ni_9 and CeY_2Ni_9 are therefore closer to that of YNi_3 as to $LaNi_3$, $CeNi_3$ or RMg_2Ni_9 compounds. Polarized neutron experiments have shown that the magnetic resurgence observed for YNi_3, among all the Y–Ni alloys, essentially arises from the Ni 3d electrons [21,22]. It can be assumed that the ferromagnetic behaviour of LaY_2Ni_9 and CeY_2Ni_9 has the same origin. A significant variation of T_C is nevertheless observed: T_C decreases upon Y by La substitution, whereas it increases upon Ce substitution. On the other hand, the saturation magnetization at 5 K is slightly larger for LaY_2Ni_9 than for CeY_2Ni_9 and YNi_3.
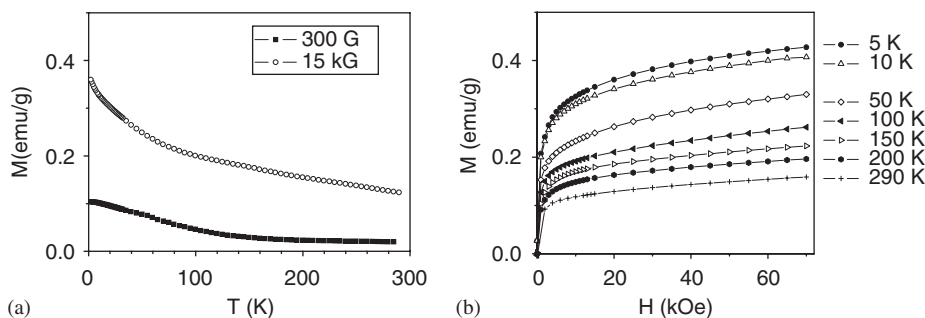
Fig. 4. Isofield (a) and isotherm (b) magnetizations of $LaY_2Ni_9H_{12}$.
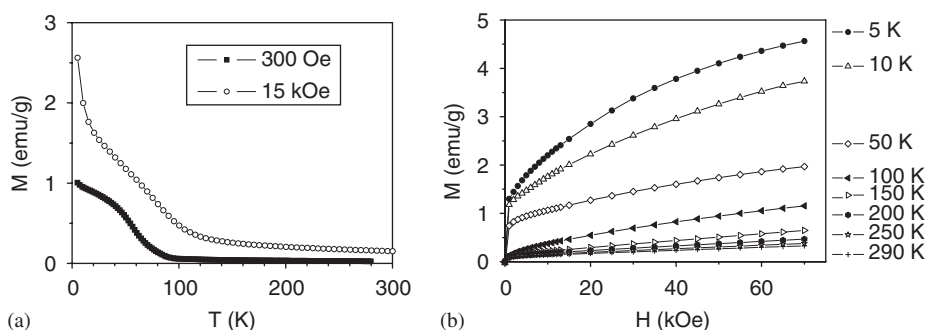
Fig. 5. Isofield (a) and isotherm (b) magnetizations of $CeY_2Ni_9H_8$.
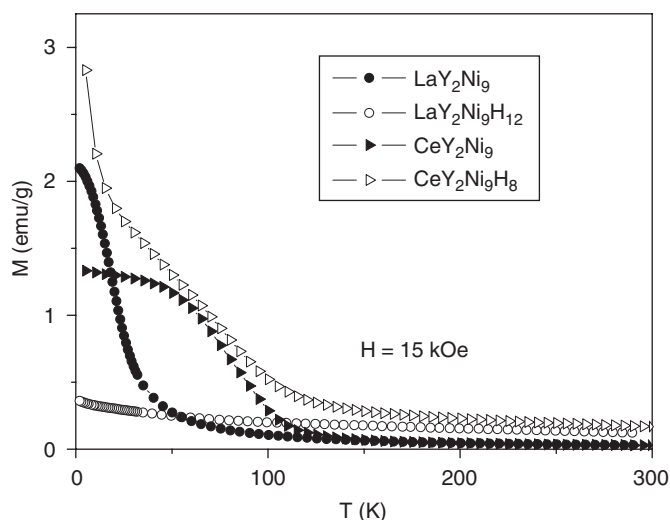
Fig. 6. Comparison of the isofield magnetization of the RY_2Ni_9 compounds and their hydrides.

CeY_2Ni_9 is isostructural to YNi_3 ($PuNi_3$ type), with a disordered Ce for Y substitution and close cell volume [6]. Band structure calculations on the Y–Ni compounds [29] have explained the resurgence of the ferromagnetism in YNi_3 and Y_2Ni_7 by the localization of the Fermi Level E_F in a sub-peak of the density of states (DOS). Compared to YNi_3, the electronic contribution of the Ce atoms in CeY_2Ni_9, with a partial filling of the $4f$ band, should modify the shape of the DOS. The larger Ni moment in CeY_2Ni_9 compared to YNi_3, is probably related to a

slightly larger DOS at E_F ($n(E_F)$). LaY_2Ni_9 crystallizes also in a trigonal $R\bar{3}m$ space group, but with a partial order of La in the $3a$ site and a larger cell volume than YNi_3 ($+2.5\%$) [6]. This should induce a better localization of the Ni $3d$ band, increases $n(E_F)$ and consequently the Ni moment according to the Stoner criterium.

Hydrogen absorption leads to different variations of the magnetic properties depending of the R element. $LaY_2Ni_9H_{12}$ behaves as an enhanced Pauli paramagnet. The loss of ferromagnetic order upon H absorption was also observed in YNi_3 hydride, YNi_3H_4 being a Pauli paramagnet [23]. This can be explained by the filling of the conduction band with the additional H electrons which contribute to the decrease of $n(E_F)$ below a critical value for the onset of ferromagnetism.

On the contrary $CeY_2Ni_9H_8$ remains ferromagnetic with an additional contribution of magnetic Ce^{3+}. The contribution of magnetic Ce has been already discussed before. The fact that this compound remains ferromagnetic can be related to the lower H content compared to YNi_3H_4 and $LaY_2Ni_9H_{12}$, since the H atoms are only located in the $MgZn_2$ units. As hydrogen absorption leads to an increase of the cell volume, the band width becomes narrower and the Ni $3d$ band is better localized. At the same time, the addition of H electrons leads to the formation of an additional sp band below E_F and then to a filling of the conduction band, which can significantly decrease $n(E_F)$ for large H content and therefore the magnetization. Such an effect has been observed and calculated for YFe_2 hydrides with H content up to 5 H/f.u. [30].

4. Conclusions

Both LaY_2Ni_9 and CeY_2Ni_9 behave as ferromagnets with Curie temperature of 15 and 92 K, respectively. The Ce atoms in CeY_2Ni_9 are non-magnetic in agreement with the fluctuating valent state observed by XAS. The magnetic properties of these compounds are strongly influenced by H absorption. $LaY_2Ni_9H_{12}$ is a Pauli paramagnet whereas $CeY_2Ni_9H_8$ remains ferromagnetic with an additional magnetic contribution of the trivalent Ce_{6c} atoms belonging to the $MgZn_2$ units. The different magnetic behaviours of these two hydrides have been related to the difference in H content, which influences significantly the filling of the conduction band.

Acknowledgments

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