Investigation of structural evolution and hydrogen sorption properties of $Y_{0.9}Ni_{2-y}Mn_y$ ($0.1 \leq y \leq 0.5$) alloys with *C*15 Laves phase structure

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INTRODUCTION

Hydride forming AB_2-type alloys with *C*15 Laves phase structure ($Fd\bar{3}m$) possess more tetrahedral sites than AB_5 and AB_n ($3 \leq n \leq 3.8$) ones to accommodate atomic hydrogen, thus higher hydrogen absorption capacity is foreseen [1] (Fig. 1).

Higher capacity
Lower stability
Poorer cycle life

AB_2 AB_3 A_2B_7 A_5B_{19} AB_5

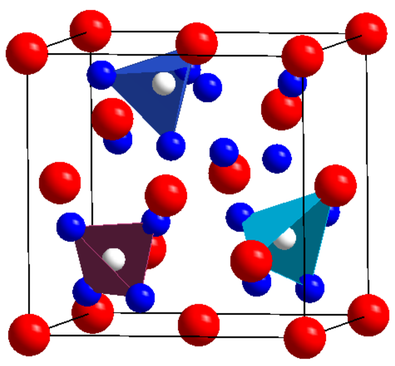
Good stability
Better cycle life
Lower capacity

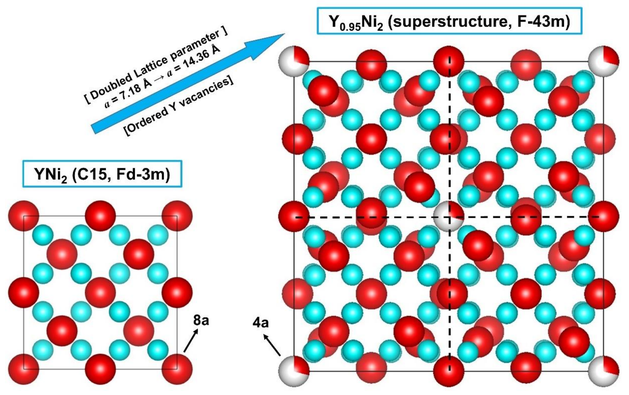
YNi_2 suffers from hydrogen-induced amorphization [2]. This work aims at stabilizing YNi_2 upon hydrogen cycling by substituting Mn for Ni in pseudo-binary $Y_{0.9}Ni_{2-y}Mn_y$ ($0.1 \leq y \leq 0.5$) compounds.

*C*15 Laves Phase structure showing tetrahedral interstitial sites for H

- **Rare earth (R)**
- **Transition metals (M)**
- **Hydrogen**

The trend of hydrogen occupy at tetrahedral sites:
96g [R2M2]>32e [RM3]>8b [M4]





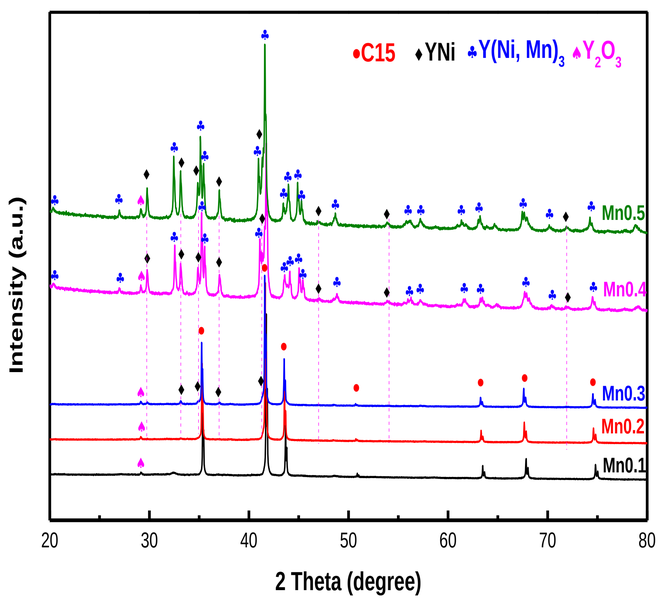
METHODS

- **Induction melting:** Nominal composition $Y_{0.9}Ni_{2-y}Mn_y$ (y = 0.1, 0.2, 0.3, 0.4, 0.5)
- **Heat treatment:** T = 1123K, t = 3 days
- **X-ray diffraction (XRD)**
- **Electron Probe Micro-Analysis (EPMA)**
- **Neutron Powder diffraction (NPD)**
- **Pressure-Composition Isotherm (PCI):** T = 423 K, Sieverts' method

Phase transformation from *C*15 Laves structure to the superstructure with ordered Y-site vacancies at 4*a* site (*F*-43*m*)

RESULTS

Phase occurrence

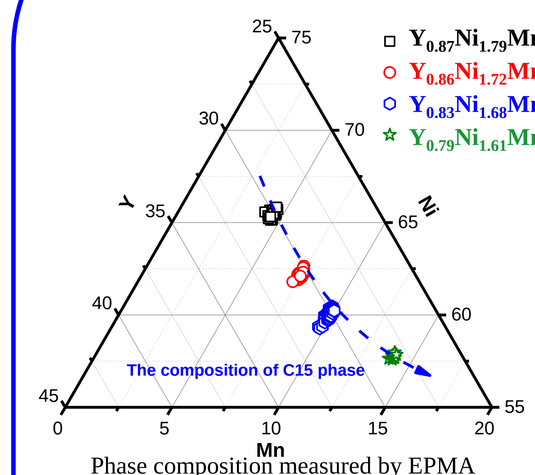


XRD patterns of $Y_{0.9}Ni_{2-y}Mn_y$ (y = 0.1, 0.2, 0.3, 0.4, 0.5) alloys

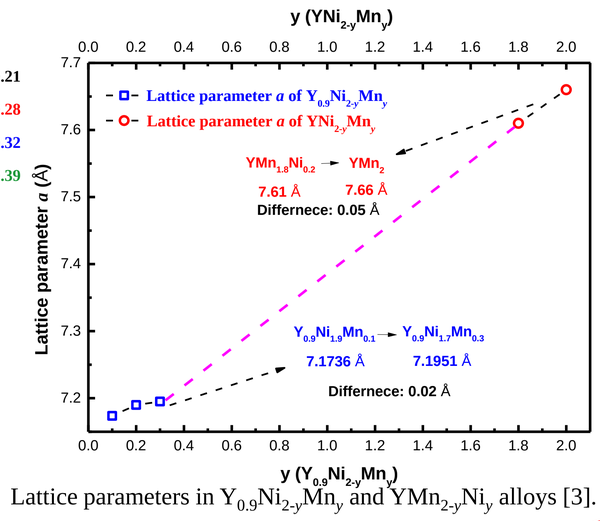
Phase	Mn0.1	Mn0.2	Mn0.3	Mn0.4	Mn0.5
***C*15**	96%	95%	90%	14%	
YNi		4%	9%	23%	27%
AB_3				62%	72%
Y_2O_3	4%	1%	1%	1%	1%

- *C*15 Laves phase is the main phase for $y \leq 0.3$ and YNi is the secondary phase. The abundance of YNi phase increases with the increasing Mn content to balance the sub-stoichiometry in the C15 phase
- $Y(Ni, Mn)_3$ forms when Mn content up to 0.4 and 0.5, which may indicate the limit of solid solution of Mn in *C*15 phase.

Structural analysis



Phase composition measured by EPMA



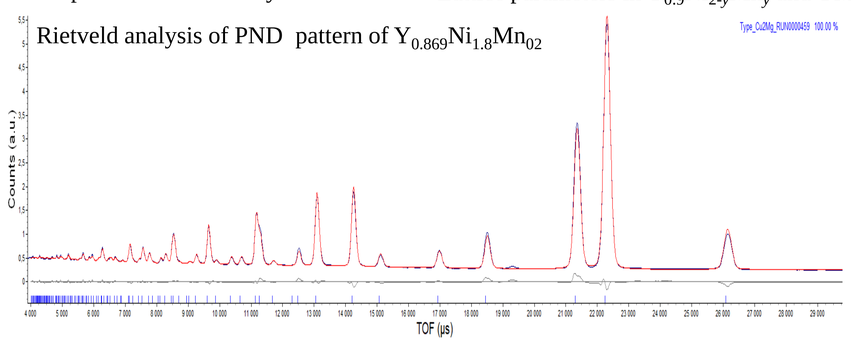
Lattice parameters in $Y_{0.9}Ni_{2-y}Mn_y$ and $YMn_{2-y}Ni_y$ alloys [3].

- EPMA analyses show Y sub-stoichiometry which increases with Mn content
- However, the lattice parameter of the *C*15 phase increases gradually with Mn content

➡ $Y_{0.9}Ni_{2-y}Mn_y$ compounds crystalize in the *C*15 structure with higher content of disordered Y-site vacancies while Mn substitutes Ni ?

The question cannot be solved by XRD since Ni and Mn cannot be differentiated

TOF Rietveld analysis of PND pattern of $Y_{0.869}Ni_{1.8}Mn_{02}$

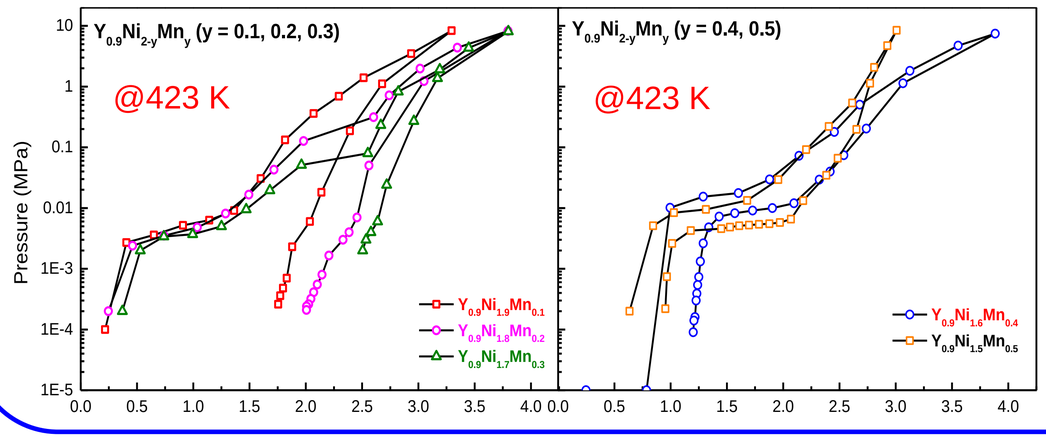


Rietveld analysis of PND data shows

- Non vacancies on the *A*-site
- Mn occupies the *B*-site as well as the *A*-site.

➡ Mn behaves both as a *A*- and *B*-type atom. This has been previously observed in $TbNi_2Mn$ and $ZrMn_{2+x}$ systems [4, 5]

Pressure-composition isotherms



- Two pressure plateaus are observed for absorption
- The first plateau pressure remains almost unchanged
- The plateau pressure of the second plateau decreases with Mn content
- The *C*15 phase still not stable upon hydrogen absorption/desorption
- Samples with Mn content between 0.4 and 0.5 show reversible hydrogen absorption due to the presence of an AB_3 phase

CONCLUSIONS

- The *C*15 Laves phase forms in the $Y_{0.9}Ni_{2-y}Mn_y$ system with large sub-stoichiometry of Y
- PND analysis indicates that the sub-stoichiometry is not due to *A*-site Y-vacancies as for $Y_{0,95}Ni_2$ but to the anti-site occupation of Mn atom.
- *C*15 phase containing Mn are not stable upon hydrogenation but AB_3 phase shows good reversibility and very small hysteresis.

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