1-1-2020

NMR studies of the ground states of Ni50-xCoxMn35In15 (x=1, 2.5) and Ni45Co5Mn37In13 Heusler alloys

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Recommended Citation

Aryal, A., Dubenko, I., Pandey, S., Chen, J., Talapatra, S., Chlan, V., Stepankova, H., Matveev, V., Blinov, M., Prudnikov, V., Granovsky, A., Lähderanta, E., Stadler, S., & Ali, N. (2020). NMR studies of the ground states of Ni50-xCoxMn35In15 (x=1, 2.5) and Ni45Co5Mn37In13 Heusler alloys. *AIP Advances, 10* (1) https://doi.org/10.1063/1.5129976

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AIP Advances

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Cite as: AIP Advances **10**, 015328 (2020); https://doi.org/10.1063/1.5129976
Submitted: 17 October 2019 • Accepted: 27 December 2019 • Published Online: 17 January 2020

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AIP Advances ARTICLE scitation.org/journal/adv

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Presented: 6 November 2019 • Submitted: 17 October 2019 •
Accepted: 27 December 2019 • Published Online: 17 January 2020

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Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials.

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ABSTRACT

Three temperature-induced phase transitions at $T=T_1$, T_M/T_A, and T_C, related to the ferromagnetic order of the martensitic phase (FMMP), martensitic (structural) transitions (MT), and the ferromagnetic order of the austenitic phase (FMAP), respectively, have been observed in the off-stoichiometric Heusler alloys, $Ni_{50-x}Co_xMn_{35}In_{15}$ (x=1, 2.5) and $Ni_{45}Co_5Mn_{37}In_{13}$. The phase transitions temperatures are found to be depended on alloy composition. A kinetic arrest of the AP was observed for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ in the magnetization measurements during field-cooling cycle (FCC) at 50 kOe. Depending upon the cooling protocols, ZFC and FCC (at H = 50 kOe), two different ground states of the alloys can be found in $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and $Ni_{45}Co_5Mn_{37}In_{13}$ alloys. The ground states (T=4.2 K and external field H=0) of the alloys was found to be characterized by three main line: two, partially overlapping, at higher frequencies (300-450 MHz), most likely corresponding of manganese resonance lines and one at lower frequency at about 200 MHz. A significant shift in the spectrum of $Ni_{45}Co_5Mn_{37}In_{13}$ by about 100 MHz to higher frequencies was observed. The correlation of magnetizations obtained from magnetic moment and NMR studies is discussed.

I. INTRODUCTION

The off-stoichiometric Mn-based Heusler alloys are intermetallic compounds described as $Ni_2Mn_{1-x}Z_x$ (Z = Ga, In, Sn, Sb.). The properties of some of these alloys are found to be sensitive to small changes in both stoichiometry and chemical composition. The differences in the resulting properties observed between these doped, off-stoichiometric, and parent Heusler alloys can be much more pronounced than those typically observed for doped metallic systems with linear monotonic changes in the behaviors depending on the concentrations of the doped elements. Thus, new magneto-responsive properties related to changes in magnetic and structural order may be observed in new doped and off-stoichiometric Heusler alloys. Alloys for which the structure and magnetic transitions happen simultaneously (so-called magneto-structural transitions) are of particular interest.

The alloys forming a ferromagnetic martensitic state (FMS) below $T=T_{CM}$, and undergo a magnetostructural (martensitic) transition (MST) from a low-magnetization martensitic state (LMS) to a ferromagnetic (FM) high-temperature austenitic phase (AP),

at T=T_A/T_M (as temperature increase/decrease), and ferromagnetic to paramagnetic transition of AP at the Curie temperature at T = T_C.

The unique combination of magnetoresponsive properties such as giant magnetoresistance,[1,2] direct and inverse magnetocaloric effects (MCE),[3,4] magnetic field induced strains,[5] magnetic shape memory effects,[6] giant anomalous Hall effects,[7] and large exchange bias[8,9] have been reported in the vicinity of the MST for off-stoichiometric Heusler alloys.

Ferromagnetic resonance (FMR) and electron spin resonance (ESR) techniques were applied to study the magnetic properties of $Ni_{49.1}Mn_{35.4}In_{15.5}$ and $Ni_{49.9}Mn_{37}Sn_{13.1}$ Heusler alloys. The results showed that the coupled ferromagnetic and antiferromagnetic interactions can be separated near and below the martensitic transition.[10] Unusually strong damping, observed in between 200-350 K, for $Ni_{45}Cr_5Mn_{37}In_{13}$ was associated with strong crystal and magnetic phase inhomogeneity, texture, and dispersion of magnetic anisotropy.[11] Such systems may demonstrate new structural, magnetic, and transport properties important for potential applications in magnetic refrigeration, spintronic, and sensors, and therefore the materials can be considered as materials for potential multi-functional applications. Despite these materials begin the subject of many numerical studies, some fundamental problems related to interrelations between structural and magnetic properties are not well understood. Therefore, this study of the MSTs using new techniques and new Heusler alloys will improve the understanding of the mechanisms responsible for MSTs in magnetic metallic systems.

In this work, we report the studies of the correlation between the magnetic and NMR properties resulting from magnetic and crystal structure heterogeneity observed in the ground states of $Ni_{50-x}Co_xMn_{35}In_{15}$ (x=1, 2.5) and $Ni_{45}Co_5Mn_{37}In_{13}$ Heusler Alloys as a consequence of the temperature induced first order magnetostructural transitions.

II. EXPERIMENTAL TECHNIQUES

Polycrystalline samples of $Ni_{50-x}Co_xMn_{35}In_{15}$ (x=1, 2.5) and $Ni_{45}Co_5Mn_{37}In_{13}$ were prepared by arc-melting 4N purity elements Ni, Mn, In, and Co in a ultra-high-purity argon atmosphere. The ingots were re-melted four times, and were annealed in high vacuum (~10^{-4} Torr) for 24 h at 850°C and slowly cooled down to room temperature. Samples with Mn differences of about 1 w.% were used for these studies. To determine the phase purities and crystal structures, X-ray diffraction (XRD) measurements were applied out with Cu-Kα radiation. The magnetic properties were measured at temperatures ranging from 10-400 K and in magnetic fields up to 5 T using a Quantum Design superconducting quantum interference device magnetometer (SQUID). The magnetization measurements were carried out during heating after the samples were cooled from 400 K to 10 K at zero or at some applied magnetic field, denoted by ZFC and FC, respectively, and during the field cooling cycle (FCC). The NMR measurements were performed by the spin-echo method with phase-coherent pulse spectrometer (Bruker Avance). NMR spectra of the alloys were recorded in the range 40-600 MHz at temperature 4.2 K without external magnetic field. The broadband NMR probe was untuned, i.e., the rf coil with the sample was dampened and not properly impedance-matched to the spectrometer. As a consequence, a non-flat frequency dependence of excitation as well as detection sensitivity is expected.

III. RESULTS AND DISCUSSION

A X-ray diffraction (XRD) patterns at 300 K indicate that the $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ sample is in mixed state that can be described as a combination of the high temperature austenitic (cubic) and low temperature martensitic (tetragonal) phases (Fig. 1). The tetragonal phases were found to dominate at room temperature for $Ni_{45}Co_5Mn_{37}In_{13,}$ (the trace of the (220) line of the cubic phase can still be visible near $(002)/(202)_T$ line). Such behavior is typical for Heusler alloys exhibiting MST, with martensitic transitions near room temperature.[12–15]

The three phase transitions clearly appeared for all studied samples (see M(T) curves for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ in Figure 2(a) as an example). These are transitions from ferromagnetic martensitic phase (FMP) to low magnetization martensitic phase (LMMP), from a LMMP to a ferromagnetic austenitic phase (FMAP) and from FMAP to a paramagnetic austenitic phase (PMAP) at T_{CM}, T_A (T_M), and T_C, respectively. The magnetizations of the FMAP and FMP were found to be strongly affected by the Co and In concentration. Large magnetizations of about 120 emu/g were detected for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and $Ni_{45}Co_5Mn_{37}In_{17}$ in the FMAP state (see Fig. 2(b)). It is interesting to note that for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ alloy no martensitic transition in the FCC curve was observed at H = 50 kOe (see Fig. 2(b)), which suggests the kinetic arrest of the AP.

The irreversibility in the FC, ZCF, and FCC magnetization curves, similar to that observed for kinetic arrest phenomena,[14] were observed for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and $Ni_{45}Co_5Mn_{37}In_{13}$ alloys at H=50 kOe (see in Figure 2(b)). Both alloys were found to be in ferromagnetic states and the magnetization isotherms shown in Figure 3. The FCC procedure with H=50 kOe results in increases of about two and four times of the magnetization of the ground state to 120 emu/g for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and 50 emu/g for $Ni_{45}Co_5Mn_{37}In_{13}$, respectively. Thus, depending on the cooling protocol, the ground states of the alloys can be different from those of the FMMP. A small increase in the magnetization of about 20 emu/g at 10 K was

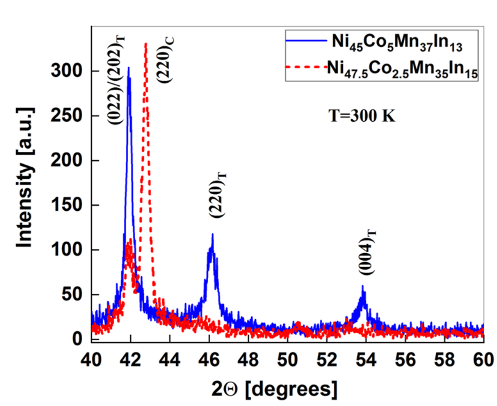

FIG. 1. XRD patterns for $Ni_{45}Co_5Mn_{37}In_{13}$ and $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$. The indexes "C" and "T" denote cubic and tetragonal Miller indexes, respectively.

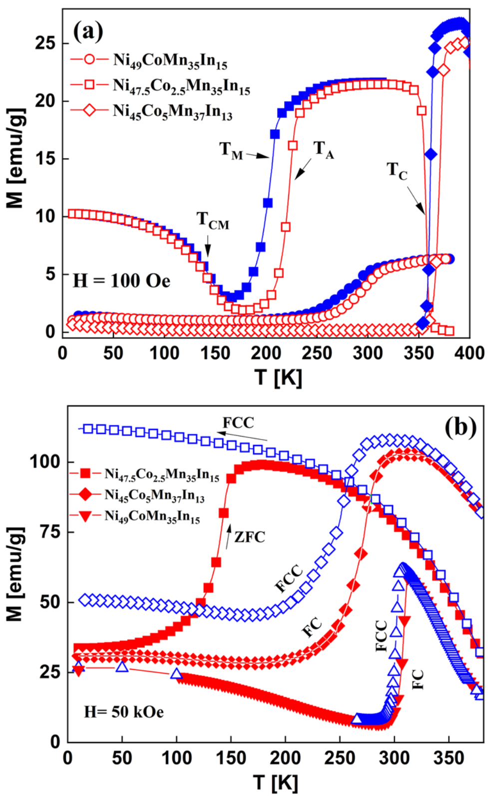

FIG. 2. The temperature dependencies of the magnetizations of Heusler alloys obtained using (a): FC and FCC protocols at H=100 Oe: and, (b): FC, ZFC, and FCC protocols at H=50 kOe. Phase transition temperatures (shown by the arrows for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$) are indicated by T_{CM}, T_A/T_M, and T_C. The M(T) curves obtained during heating and cooling are plotted using red and blue symbols, respectively.

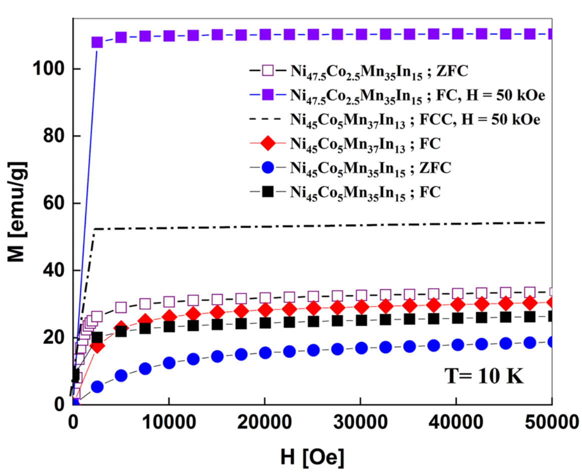

FIG. 3. ZFC and FC magnetization isotherms of the compounds at 10 K.

observed for $Ni_{45}Co_5Mn_{37}In_{13}$ after the samples were cooled down from 380 to 10K at H=50 kOe. The result shows that the FMAP in $Ni_{45}Co_5Mn_{37}In_{13}$ can also be stabilized by the application of the magnetic field.

NMR spectra of some Heusler alloys are shown in Figure 4. As one can see the spectra (T=4.2 K and external field H=0) they are characterized by three main lines: one at low frequency (~ 100-200 MHz), and two in a higher frequency interval of about (300-450) MHz. The two high-frequency lines almost fully overlap for $Ni_{49}CoMn_{35}In_{15}$ in interval (200-450) MHz and clearly separated in case of $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and $Ni_{45}Co_5Mn_{37}In_{13}$.

The high frequency lines most likely correspond to Mn atoms that occupy crystal cell positions in the off stoichiometric Heusler alloys. Considering that magnetic moment of Ni is rather low in these types of compounds [see in Ref. 1], the low-frequency line is most likely linked with the Ni magnetic moment. A significant shift of the spectrum of $Ni_{45}Co_5Mn_{37}In_{13}$ by about 100 MHz to higher frequencies was observed. Thus, taking into account that the configuration of the nearest atoms is not changed at the martensitic transition, the observed shift of the spectra to high frequency is most likely related to the difference between the cell volume of the AP and MP, since NMR (roughly) follows the effective magnetic fields created by the surrounding magnetic atoms.

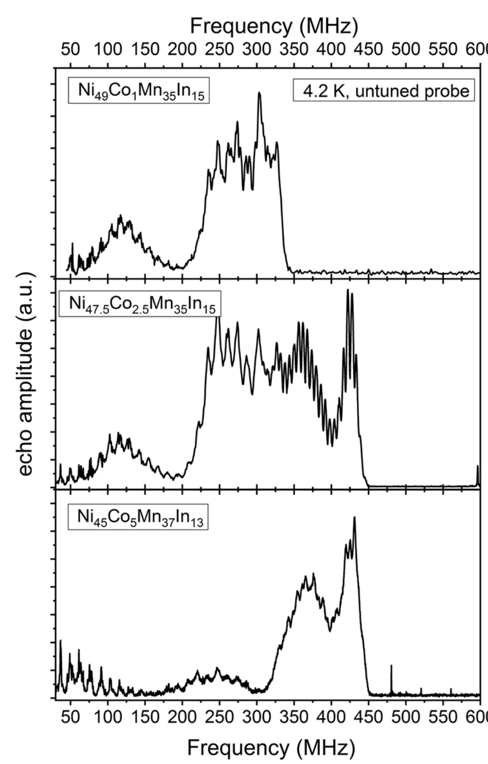

FIG. 4. NMR spectra obtained for characteristic Heusler alloys after samples were cooling in presence of magnetic fields. The oscillations (~ 14 MHz) are artificial and caused by the standing waves produced within the coaxial line due to a poorly matched rf coil. No correction to the frequency dependence of sensitivity was performed.

IV. CONCLUSIONS

The correlation between the magnetic and NMR properties resulting from magnetic and crystal structure heterogeneity observed in the ground states of off-stoichiometric $Ni_{50-x}Co_xMn_{35}In_{15}$ (x=1, 2.5) and $Ni_{45}Co_5Mn_{37}In_{13}$ Heusler Alloys as a consequence of the temperature induced first order MST has been studied. Magnetization results show three temperature-induced phase transitions at $T=T_1$, T_M/T_A, and T_C, related FMMP, MST, and the FMAP, respectively, in these Heusler Alloys. A kinetic arrest of the AP during the martensitic transition was observed for $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ in the magnetization measurements during field-cooling cycle (FCC) at 50 kOe. Two different ground states were found in $Ni_{47.5}Co_{2.5}Mn_{35}In_{15}$ and $Ni_{45}Co_5Mn_{37}In_{13}$ alloys depending upon the cooling protocols. In NMR spectra, ground states (T=4.2 K and external field H=0) of the alloys was found to be characterized by three main line: two, partially overlapping, at higher frequencies (300-450 MHz), most likely corresponding of manganese resonance lines and one at lower frequency at about 200 MHz. A significant shift in the spectrum of $Ni_{45}Co_5Mn_{37}In_{13}$ by about 100 MHz to higher frequencies was observed that could result from different cell volume of AP and MP.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences Award No. DE-FG02-06ER46291 (SIUC) and DE-FG02-13ER46946 (LSU). This work was partly supported by Academy of Finland, grant number 318405.

REFERENCES

[1] S. Y. Yu, Z. H. Liu, G. D. Liu, J. L. Chen, Z. X. Cao, G. H. Wu, B. Zhang, and X. X. Zhang, Appl. Phys. Lett. **89**, 162503 (2006).
[2] M. Khan, A. K. Pathak, M. R. Paudel, I. Dubenko, S. Stadler, and N. Ali, J. Magn. Magn. Mater. **320**, L21 (2008).
[3] A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Appl. Phys. **93**, 4722 (2003).
[4] O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[5] J. Du, Q. Zheng, W. J. Ren, W. J. Feng, X. G. Liu, and Z. D. Zhang, J. Phys. D: Appl. Phys. **40**, 5523–5526 (2007).
[6] Z. D. Han, D. H. Wang, C. L. Zhang, S. L. Tang, B. X. Gu, and Y. W. Du, Appl. Phys. Lett. **89**, 182507 (2006).
[7] I. Dubenko, A. K. Pathak, S. Stadler, N. Ali, Ya. Kovarskii, V. N. Prudnikov, N. S. Perov, and A. B. Granovsky, Phys. Rev. B **80**, 092408 (2009).
[8] M. Khan, I. Dubenko, S. Stadler, and N. Ali, Appl. Phys. Lett. **91**, 072510 (2007).
[9] A. K. Pathak, M. Khan, B. R. Gautam, I. Dubenko, S. Stadler, and N. Ali, J. Magn. Magn. Mater. **321**, 963–965 (2009).
[10] S. Aksoy *et al.*, Journal of Physics: Conference Series **200**, 092001 (2010).
[11] S. Pandey, S. Vyzulin, A. Quetz, A. Aryal, I. Dubenko, A. Granovsky, S. Stadler, and N. Ali, AIP Advances **8**, 056707 (2018).
[12] I. Dubenko, T. Samanta, A. Kumar Pathak, A. Kazakov, V. Prudnikov, S. Stadler, A. Granovsky, A. Zhukov, and N. Ali, J. Magn. Magn. Mater. **324**, 3530–3534 (2012).
[13] S. Pandey, A. Quetz, I. D. Rodionov, A. Aryal, M. I. Blinov, I. S. Titov, V. N. Prudnikov, A. B. Granovsky, I. Dubenko, S. Stadler, and N. Ali, J. Appl. Phys. **117**, 183905 (2015).
[14] W. Ito, K. Ito, R. Kainuma, A. Fujita, K. Oikawa, K. Ishida, and T. Kanomata, Appl. Phys. Lett. **92**, 021908 (2008).
[15] S. Roy, E. Blackburn, S. M. Valvidares, M. R. Fitzsimmons, S. C. Vogel, M. Khan, I. Dubenko, S. Stadler, N. Ali, S. K. Sinha, and J. B. Kortright, Phys. Rev. B **79**(1-5), 235127 (2009).