

Phase formation characteristics and magnetic properties of bulk Ni₂MnGe Heusler alloy

U. Adem,¹ İ. Dinçer,¹ S. Aktürk,² M. Acet,³ and Y. Elerman¹

¹*Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Besevler, Ankara, Turkey*

²*Department of Physics, Faculty of Sciences and Letters, Muğla University, 48000 Kötekli, Muğla, Turkey*

³*Experimental Physics, Duisburg-Essen University, 47048 Duisburg, German*

(Dated: August 20, 2014)

We have systemically studied the effects of annealing temperature and alloy composition on the structural and magnetic properties of bulk Ni₂MnGe and Ni_{2.1}Mn_{0.9}Ge Heusler alloys. We have observed that both annealing temperature and the alloy composition drastically alter the phases found in the samples due to the presence of competing ternary phases. Annealing at 900 and 950 °C for both alloy compositions facilitate the formation of L2₁ Heusler phase. Nevertheless, formation of Ni₅Mn₄Ge₃ and Ni₁₆Mn₆Ge₇ phases cannot be prevented for Ni₂MnGe and Ni_{2.1}Mn_{0.9}Ge alloys, respectively. In order to estimate the magnetic contribution of the Ni₅Mn₄Ge₃ impurity phase to that of the parent Ni₂MnGe, we have also synthesized pure Ni₅Mn₄Ge₃ alloy. Antiferromagnetic nature of Ni₅Mn₄Ge₃ with low magnetization response allows us to reveal the magnetic response of the stoichiometric bulk Ni₂MnGe. Bulk Ni₂MnGe shows simple ferromagnetic behavior with a Curie temperature of 300 K, in agreement with the previous results on thin films. Despite the divergence of magnetization curves between field cooled (FC) and field heated (FH) modes, stoichiometric Ni₂MnGe alloy does not undergo a martensitic phase transition based on our variable temperature x-ray diffraction experiments.

PACS numbers:

Ni-Mn based Heusler alloys constitute a prime family of compounds that have been studied extensively due to the presence of a magnetostructural phase transition which makes them useful for magnetic refrigeration and magnetic shape memory applications such as actuators¹⁻³. Upon cooling, Ni-Mn-Z (where Z = Ga, In, Sn, Sb) undergo a phase transition into a martensitic phase. Only for Ni₂MnGa phase, martensitic phase transition occurs for the stoichiometric Heusler composition in the ferromagnetic state. Associated with the first order martensitic phase transition, (magnetic) shape memory effects are observed in these alloys. Magnetic and structural phase transition temperatures can be tailored to yield large caloric effects, which makes them useful for magnetic refrigeration applications¹.

Despite the abundance of studies on other Heusler compositions, there have been relatively few studies on Ni₂MnGe both in bulk and thin film form. Lund et al. have reported the growth of thin films of Ni₂MnGe using Molecular Beam Epitaxy (MBE) and obtained ferromagnetic films with a Curie temperature of 300 K⁴. Kim et al. have grown Ni₂MnGe films using flash evaporation. Their films were ferromagnetic with a Curie temperature of 280 K⁵. Only Oksenenko et al. have reported the structural and magnetic properties of stoichiometric bulk Heusler composition Ni₂MnGe⁶. They could not obtain a pure Heusler phase and observed complex magnetization behaviour accordingly. Si et al. synthesized bulk Ni_{2.1}Mn_{0.9}Ge and Ni_{2.2}Mn_{0.8}Ge⁷. They claimed to obtain pure off-stoichiometric Heusler phase. Their magnetic measurements show a simple ferromagnetic be-

havior with an ordering temperature T_C of 246 K for Ni_{2.1}Mn_{0.9}Ge and 151 K for Ni_{2.2}Mn_{0.8}Ge.

The key property that renders other Ni-Mn based Heusler alloys useful for applications is the presence of a first-order martensitic phase transition from high temperature L2₁ phase to a low temperature martensite phase¹. Zayak et al. predicted an instability of L2₁ structure in Ni₂MnGe alloys using first-principles calculations but this has not been observed so far⁸. Recently, there has been another prediction⁹, suggesting the likelihood of a transition from the cubic austenite phase to a tetragonal martensite phase. We have undertaken a systematic study to clarify the structural and magnetic properties of stoichiometric bulk Ni₂MnGe and to address the martensitic phase transition predictions. In addition to the stoichiometric composition, we have also synthesized Ni_{2.1}Mn_{0.9}Ge alloy, in order to reproduce the pure L2₁ Heusler phase claimed in ref.⁷. Another off-stoichiometric sample with the determined composition of Ni_{1.91}Mn_{0.94}Ge_{1.15} was also used to study the effect of Ni off-stoichiometry and demonstrate the effect of annealing temperature. We have observed that annealing temperature and alloy composition significantly affect the phases encountered in the alloys. Finally, we show the lack of a martensitic phase transition using variable temperature x-ray diffraction experiments.

I. EXPERIMENTAL

Ni_2MnGe , $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$, $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ and $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ alloys were synthesized by arc-melting the constituting elements under Ar atmosphere using an Arc Melter. The alloys were melted 5 times to assure melt homogeneity. Ni_2MnGe and $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ alloys were annealed first at 900°C for 3 days in order to reproduce the synthesis conditions in ref.⁷ and then subsequently annealed at 950 °C for 4 days to see the effects of higher temperature on the stability of phases. $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ alloy was annealed at 800°C for 6 days following ref.¹⁰. $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ was annealed at 800°C for a week and then subsequently annealed at 950°C for another week. Annealing was done with samples closed in quartz tubes under Ar atmosphere and alloys were quenched in ice water. Composition of the alloys were checked using Energy Dispersive X-ray Spectroscopy(EDS) with a Zeiss EVO 40 Scanning Electron Microscope (SEM). Crystal structure of the alloys were determined using x-ray diffraction experiments with a Rigaku D-Max 2200 diffractometer with Mo K-alpha radiation at room temperature. Variable temperature x-ray diffraction experiments were carried out using a Rigaku Smartlab diffractometer having a Cu K-alpha source equipped with a commercial temperature attachment, between 83-573 K. Le Bail fits to the x-ray diffraction data were done using GSAS software package¹¹. Magnetization of the samples were measured in a MPMS magnetometer between 10-380 K.

II. RESULTS AND DISCUSSION

Fig. 1 shows the Le Bail fit of the x-ray diffraction data of the stoichiometric Ni_2MnGe alloy annealed at 900 °C for 3 days collected at room temperature. All peaks can be indexed with Heusler $\text{L}_2\text{1}$ phase with the space group $\text{Fm}\bar{3}\text{m}$ and $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ impurity phase. $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ is reported to crystallize in hexagonal $\text{P6}_3/\text{mmc}$ space group¹⁰. Lattice parameters from the Le Bail fit were obtained as $a = 5.8224(4)\text{\AA}$ for the cubic Ni_2MnGe phase and $a = 4.9288(9)\text{\AA}$ and $c = 7.680(3)\text{\AA}$ for the $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ phase, respectively. Upon further annealing at 950 °C for 4 days, $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ peaks lose their intensity (shown in the inset of Fig. 1), however a pure Ni_2MnGe phase cannot be obtained.

In Fig. 2(a), Backscattered Electron (BSD) image of Ni_2MnGe alloy is shown. There are thin dark regions within the lightly colored matrix. Point analysis from dark regions show a stoichiometry close to $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ in agreement with the XRD data. Neighbouring lightly colored regions show stoichiometric Ni_2MnGe composition (Table 1).

Le Bail fit of the x-ray diffraction data of $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ annealed at 900 °C shown in Fig. 3 can be indexed using a mixture of $\text{L}_2\text{1}$ Ni_2MnGe Heusler phase together with $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$. $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase is cubic with the

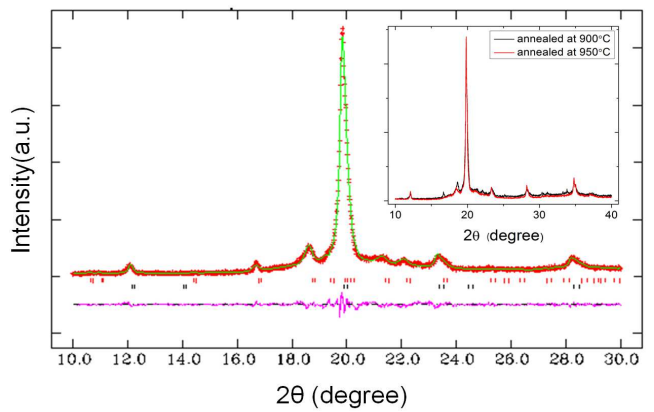


FIG. 1: X-ray diffraction pattern of Ni_2MnGe sample annealed at 900 °C for 3 days. Black ticks denote $\text{L}_2\text{1}$ Heusler peaks whereas red ticks show $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ impurity phase. Observed data is red, calculated is in green and the difference is in pink. The inset shows a comparison of the diffraction patterns corresponding to the sample annealed at 900 °C and subsequently at 950 °C.

Composition	Ni	Mn	Ge
Ni_2MnGe (dark regions)	45.83 (41.7)	31.45 (33.3)	22.72 (25)
Ni_2MnGe (light regions)	49.83 (50)	25.42 (25)	24.75 (25)
$\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$	51.91 (52.5)	22.81 (22.5)	25.27 (25)
$\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$	47.8 (47.8)	23.5 (23.5)	28.7 (28.7)

TABLE I: Elemental analysis results of Ni_2MnGe (dark regions), Ni_2MnGe (light regions), $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ and $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$. The numbers in parenthesis denote the expected values for the respective phases: i.e. $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ stoichiometry for Ni_2MnGe (dark regions), Ni_2MnGe stoichiometry for Ni_2MnGe (light regions) and $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ stoichiometry for $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$.

space group $\text{Fm}\bar{3}\text{m}$ ¹⁰. Refined lattice parameters were $a = 5.7881(5)\text{\AA}$ and $a = 11.4164(6)\text{\AA}$ for Ni_2MnGe and $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$, respectively. Further annealing at 950 °C doesn't change the stability of the phases.

In Fig. 2(b), BSD image of $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ alloy is shown. Unlike the case in Ni_2MnGe composition, no dark and lightly colored regions could be observed, therefore the presence of a second phase with $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ stoichiometry couldn't be verified. On the other hand, elemental analysis from a large area showed that the target composition has been obtained (Table 1).

In Fig. 4, we show the temperature dependence of magnetization of Ni_2MnGe , $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ and $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ samples measured at 50 Oe. Sharp increase in magnetization in both FC and FH modes define the ferromagnetic Curie temperature as 300 K for Ni_2MnGe and 320 K for $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$. There is divergence between FC and FH modes, hinting the possibility of the presence of a first order martensitic phase transition. In order to quantify the contribution of $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ im-

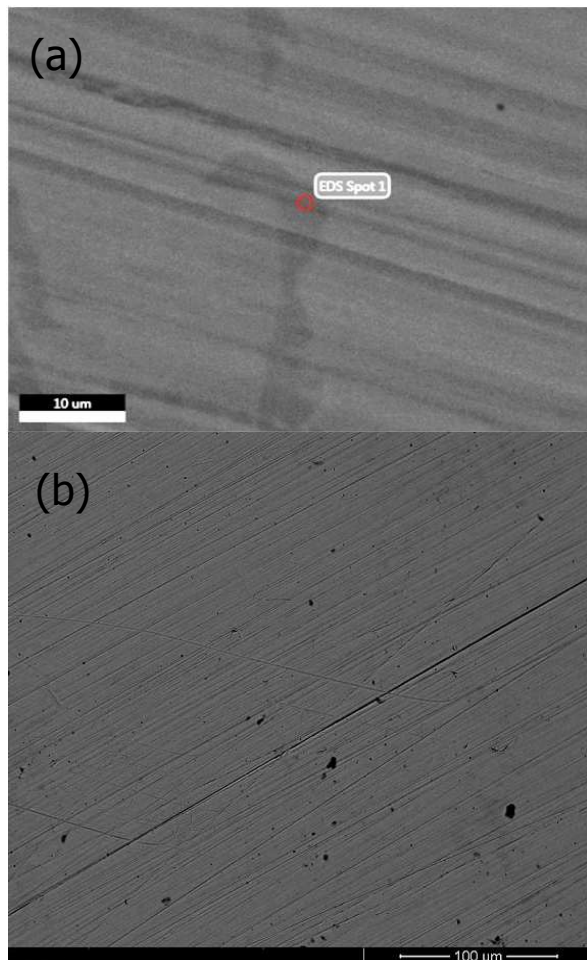


FIG. 2: Backscattered Electron (BSD) SEM images of (a) Ni_2MnGe alloy, annealed at 900°C for 3 days. Figure shows a zoomed-in region where dark colored $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ phase can be seen, surrounded by the lighter colored regions of Ni_2MnGe phase, (b) $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ alloy, annealed at 900°C for 3 days.

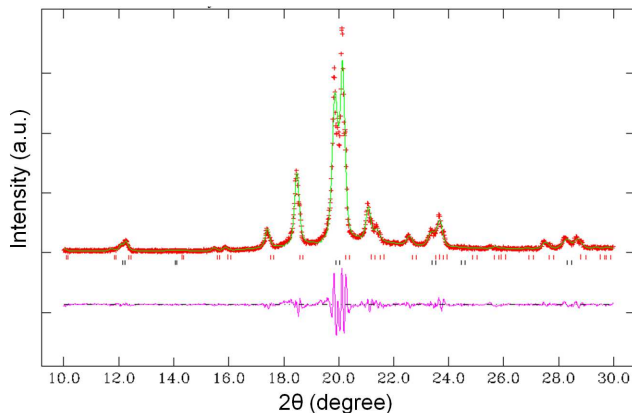


FIG. 3: Le Bail fit of the x-ray diffraction pattern of $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ sample annealed at 900°C for 3 days. Black ticks denote L_{21} Heusler peaks whereas red ticks show $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$ impurity phase.

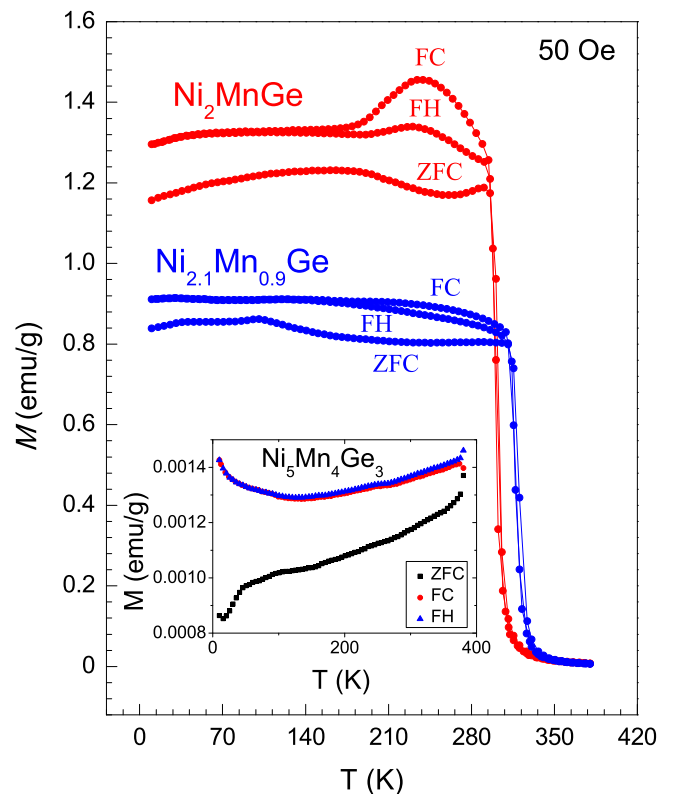


FIG. 4: Temperature dependence of magnetization of Ni_2MnGe , $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ and $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ measured at 50 Oe.

purity to the magnetic behaviour of Ni_2MnGe , a pristine $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ alloy was synthesized. Le Bail fit of XRD data of $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ alloy is shown in Fig. 5. Refined lattice parameters are $a = 4.8865(3)\text{\AA}$ and $c = 7.6662(7)\text{\AA}$. Temperature dependence of magnetization of pure $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ is shown in the inset of Fig. 4. $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ shows complex magnetic response, dominantly antiferromagnetic, however since the magnitude of magnetization is very small, magnetic contribution of $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ to the behavior of parent Ni_2MnGe is negligible.

Our studies show that $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ alloy contains two phases: L_{21} Ni_2MnGe Heusler phase and $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ (Fig. 3). Si et al. however claim that they observe only L_{21} Heusler phase⁷. Magnetic properties of $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ are unknown but provided that it shows dominantly antiferromagnetic properties similar to $\text{Ni}_5\text{Mn}_4\text{Ge}_3$, simple ferromagnetic behaviour that Si et al. have reported, assigned to L_{21} Heusler phase, can be understood.

Observation of three ternary phases (Ni_2MnGe , $\text{Mn}_6\text{Ni}_{16}\text{Si}_7$ and $\text{Ni}_5\text{Mn}_4\text{Ge}_3$) in a narrow composition range might seem unusual when one considers the number of ternary phases in Ni-Mn-Ga (only one)¹² however formation of quite a few ternary phases are known for both Ni-Mn-Ge¹⁰ and Ni-Mn-Si systems¹³. Ni-Mn-Si ternary phase diagram hosts many ternary phases, including $\text{Mn}_6\text{Ni}_{16}\text{Si}_7$ ^{13,14}. In the following, we will show

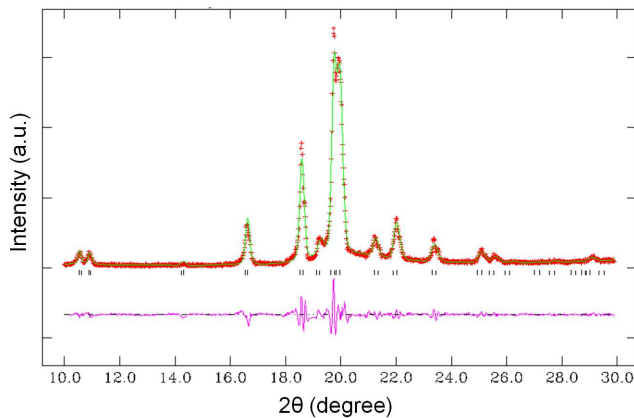


FIG. 5: Le Bail fit of x-ray diffraction pattern for $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ sample. All peaks correspond to $\text{Ni}_5\text{Mn}_4\text{Ge}_3$.

that annealing temperature plays a crucial role for the formation of Heusler phase. We have observed a very similar magnetic behavior to that in Oksenenko et al., in a Mn and Ni deficient composition, $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$, when the sample was annealed at 800°C , not at 900 or 950°C . Temperature dependence of magnetization of this alloy is shown in Fig. 6(a). There are multiple anomalies, which probably correspond to different magnetic ordering phenomena. The different and complex magnetic behavior that we observed can be ascribed to the different phases present in this alloy. Different to the Ni_2MnGe and $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$ compositions, $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ annealed at 800°C doesn't contain L_{21} Heusler phase but includes $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ and $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ phases. In Fig. 7, Le Bail fit of the X-ray diffraction pattern of $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ annealed at 800°C is shown. Black tickmarks denote peaks belonging to $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ phase, with the refined lattice parameters $a = 4.8944(3)\text{\AA}$ and $c = 7.683(2)\text{\AA}$, while red tickmarks correspond to $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase, with the refined cubic lattice parameter $a = 11.526(1)\text{\AA}$. More experiments are necessary to understand the magnetic anomalies in this alloy.

Annealing $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ composition further at 950°C yields a mixture of L_{21} Heusler Ni_2MnGe phase with $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ present as the second phase (Fig. 7). Refined lattice parameters were $a = 5.8115(2)\text{\AA}$ for the Ni_2MnGe phase and $a = 11.475(2)\text{\AA}$ for $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$. Temperature dependence of magnetization of this alloy annealed at 950°C is given in Fig. 6(b). Due to dominant presence of cubic Heusler phase, magnetization shows ferromagnetic ordering around 315 K , similar to the stoichiometric Ni_2MnGe alloy as well as to off-stoichiometric $\text{Ni}_{2.1}\text{Mn}_{0.9}\text{Ge}$, both containing cubic Heusler phases, as shown in the Fig. 4.

Another major outcome of our study is the observation of absence of a martensitic phase transition. As it has been discussed in the introduction section, there are theoretical calculations claiming the presence a structural instability in stoichiometric Ni_2MnGe that can result in a

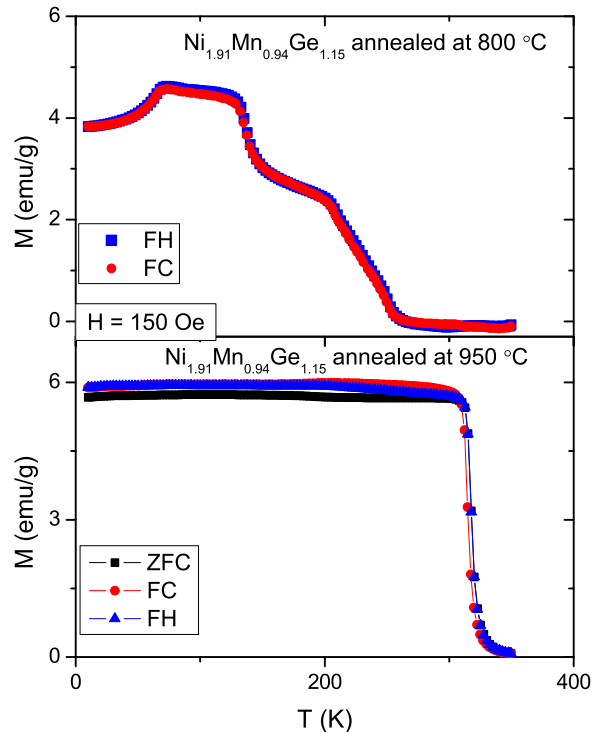


FIG. 6: Temperature dependence of magnetization of $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ sample (a) annealed at 800°C , (b) annealed at 950°C , both measured at 150 Oe .

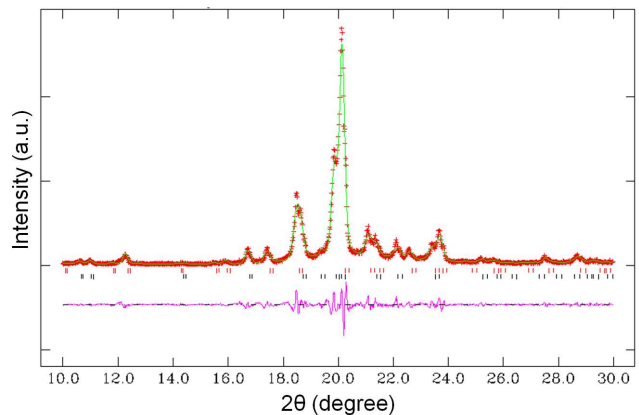


FIG. 7: Le Bail fit of the x-ray diffraction data for $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ annealed at 800°C . Black tickmarks denote $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ peaks, while red tickmarks correspond to $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase.

martensitic phase transition^{8,9}. We are able to assess this prediction satisfactorily by identifying the phases present in our samples. We have used $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ sample annealed at 950°C for this purpose. Refined diffraction pattern collected at RT was shown in Fig. 8. X-ray diffraction spectra of $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ sample, collected at 83 K , RT , 423 K and 573 K are shown in

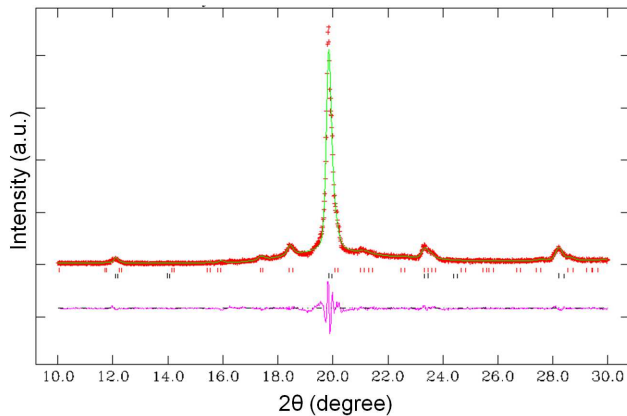


FIG. 8: Le Bail fit of the x-ray diffraction data for $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ subsequently annealed at 950°C after annealing at 800°C . Black tickmarks denote $\text{L2}_1 \text{Ni}_2\text{MnGe}$ peaks, while red tickmarks correspond to $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase.

Fig. 9. Throughout this temperature range, including the part where a divergence between FC and FH curves in magnetization was observed, both cubic Heusler peaks and peaks belonging to $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase have been observed, with no additional peaks appearing. Therefore, we conclude that no martensitic transition takes place for the stoichiometric Ni_2MnGe alloy. An additional reflection corresponding to (420) plane, belonging to the cubic Heusler phase is visible at all temperatures, different than the data collected at RT with Mo-source lab x-ray diffractometer. This might be due to the different data collection times. The lack of a structural martensitic phase transition is surprising. Typically, a divergence in magnetization between FC and FH modes of magnetization originates from a structural phase transition. Lack of a structural phase transition in our case suggests a magnetic origin for the divergence between FC and FH modes. Neutron diffraction experiments are necessary to reveal the origin of the divergence between FC and FH modes. The lack of martensitic phase transition is supporting the previous results on Ge substitution in $\text{Ni}_2\text{MnGa}_{1-x}\text{Ge}_x$ ¹⁵. For $x = 0.4$, it was reported that martensitic transition temperature decreased from 200 K to 50 K compared to the Ni_2MnGa , suggesting the suppression effect of Ge on the martensitic phase transition.

III. CONCLUSIONS

In conclusion, we synthesized alloy compositions close to the stoichiometric Heusler Ni_2MnGe and observed

that in a narrow composition range, there are two other thermodynamically stable phases in addition to the $\text{L2}_1 \text{Ni}_2\text{MnGe}$ structure: $\text{Ni}_5\text{Mn}_4\text{Ge}_3$ and $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$. By estimating the contribution from these phases, we have measured the intrinsic magnetic response of bulk Ni_2MnGe , addressing the inconsistency in previous re-

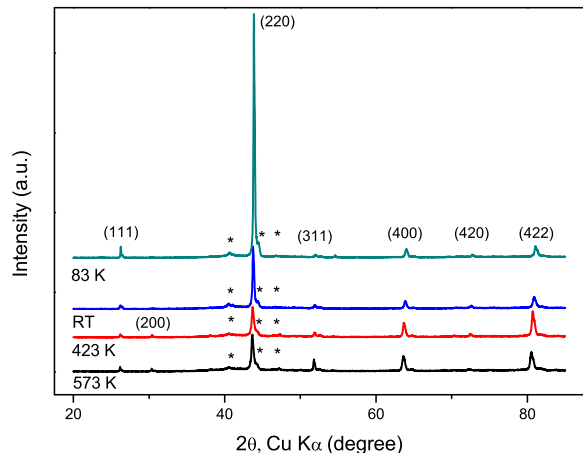


FIG. 9: X-ray diffraction spectrum of $\text{Ni}_{1.91}\text{Mn}_{0.94}\text{Ge}_{1.15}$ sample annealed at 950°C for 6 days, collected at 83 K, RT, 423 K and 573 K. Star symbols denote the reflections belonging to the $\text{Mn}_6\text{Ni}_{16}\text{Ge}_7$ phase; the rest of the reflections belong to the parent Ni_2MnGe phase.

ports. This also allowed us to evaluate the presence of a martensitic phase transition. We conclude from our variable temperature x-ray diffraction measurements that no martensitic phase transition takes place at the stoichiometric Heusler composition Ni_2MnGe . Due to the presence of various thermodynamically stable phases in equilibrium, forcing a martensitic phase transition by moving to an off-stoichiometric composition would be unlikely.

Acknowledgments

U. A. acknowledges E. Duman for helpful discussions and the financial support of Turkish Scientific and Technological Research Council (TÜBİTAK) via 2232 Programme.

¹ A. Planes, L. Manosa, and M. Acet, *Journal of Physics Condensed Matter* **21**, 233201 (2009).

² J. Liu, T. Gottschall, K. P. Skokov, J. D. Moore, and O. Gutflisch, *Nature Materials* **11**, 620 (2012).

- ³ K. Ullakko, J. K. Huang, C. Kantner, R. C. O'Handley, and V. V. Kokorin, *Applied Physics Letters* **69**, 1966 (1996).
- ⁴ M. S. Lund, J. W. Dong, J. Lu, X. Y. Dong, C. J. Palmstrom, and C. Leighton, *Applied Physics Letters* **80**, 4798 (2002).
- ⁵ R. J. Kim, N. N. Lee, B. J. Kim, Y. P. Lee, Y. Kudryavtsev, and K. W. Kim, *IEEE Transactions on Magnetics* **41**, 0018 (2005).
- ⁶ V. A. Oksenenko, L. N. Trofimova, Y. N. Petrov, Y. V. Kudryavtsev, J. Dubowik, and Y. P. Lee, *Journal of Applied Physics* **99**, 063902 (2006).
- ⁷ P. Z. Si, J. J. Liu, C. Q. Chen, Q. Wu, Z. W. Jiao, and H. L. Ge, *Journal of Alloys and Compounds* **462**, 1 (2008).
- ⁸ A. T. Zayak, W. A. Adeagbo, P. Entel, and K. M. Rabe, *Applied Physics Letters* **88**, 111903 (2006).
- ⁹ H. Luo, F. Meng, G. Liu, H. Liu, P. Jia, E. Liu, W. Wang, and G. Wu, *Intermetallics* **38**, 139 (2013).
- ¹⁰ Y. V. Kuzma, M. Y. Teslyuk, and E. I. Gladyshevskii, *Journal of Structural Chemistry* **3**, 143 (1962).
- ¹¹ A. Larson and R. V. Dreele, Los Alamos National Laboratory Report LAUR **86**, 748 (2000).
- ¹² K. Gupta, *Journal of Phase Equilibria and Diffusion* **29**, 101 (2008), ISSN 1547-7037, URL <http://dx.doi.org/10.1007/s11669-007-9017-x>.
- ¹³ K. Gupta, *Journal of Phase Equilibria and Diffusion* **27**, 529 (2006), ISSN 1547-7037, URL <http://dx.doi.org/10.1007/BF02736466>.
- ¹⁴ M. Kolenda, A. Szytula, J. Leciejewicz, and C. Maletka, *Journal of Magnetism and Magnetic Materials* **96**, 121 (1991).
- ¹⁵ I. Gościańska, J. Dubowik, Y. V. Kudryavtsev, and A. Jezierski, *Phys. Stat. Sol. (c)* **3**, 147 (2006).