5-2005

The Structural and Magnetic Properties of Ni2Mn1−xMxGa (M = Co, Cu)

Mahmud Khan
Southern Illinois University Carbondale

Igor Dubenko
Southern Illinois University Carbondale

Shane Stadler
Southern Illinois University Carbondale

Naushad Ali
Southern Illinois University Carbondale

Published in *Journal of Applied Physics*, Vol. 97 No. 10 (2005) at doi: 10.1063/1.1847131

The structural and magnetic properties of $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu)

Mahmud Khan,[a] Igor Dubenko, Shane Stadler, and Naushad Ali
Department of Physics, Southern Illinois University, Carbondale, Illinois 62901

(Presented on 8 November 2004; published online 13 May 2005)

In Ni_2MnGa (cubic structure of $L2_1$ type) a first order martensitic structural transition, from the parent cubic (austenitic) phase to a low temperature complex tetragonal structure, takes place at $T_M=202$ K, and ferromagnetic order in the austenitic phase sets at $T_C=376$ K. In this work, the Mn sites in Ni_2MnGa have been partially substituted with magnetic Co and nonmagnetic Cu, and the influence of these substitutions on the structural and magnetic properties of $Ni_2Mn_{1-x}M_xGa$ (M=Co and Cu) have been studied by XRD and magnetization measurements. X-ray diffraction patterns indicate that the Co doped system possess a highly ordered Heusler alloy $L2_1$ type structure for $0.05<x<0.12$, and the Cu doped compounds possess $L2_1$ structure for $0.05<x<0.10$. The ferromagnetic ordering temperature increases with increasing Co concentration for this system, and rapidly decreases with increasing Cu concentration. Both systems show the increase in T_M with increasing Co and Cu concentration. (T-x) phase diagrams have been plotted. The results are discussed in terms of 3*d*-electron concentration variation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1847131]

INTRODUCTION

Stoichiometric Ni_2MnGa has an $L2_1$ crystal structure at room temperature. In this alloy a first-order martensitic structural transition, from the parent cubic (austenitic) phase to a low temperature (LT) complex tetragonal structure, takes place at $T_M=202$ K, and ferromagnetic order sets in at $T_C=376$ K.[1] A steplike variation of the magnetization, magnetic susceptibility, magnetostriction, and resistivity has been observed in this system at the martensitic transition.[2,3] Positive and negative volume anomalies were also found to accompany the transitions from ferromagnetic austenitic and paramagnetic austenitic to martensitic phases, respectively.[4] The values of T_M and T_C vary significantly with the chemical composition. The partial substitution of Mn with Ni results in an increase of T_M and a decrease of T_C and, at some critical concentration, T_M and T_C coincide.[5] On the other hand, substituting Mn with Fe results in a decrease of T_M and an increase of T_C.[6] The increase of T_C with increasing pressure was found in Mn containing Heusler alloys from hydrostatic pressure experiments.[7]

It was conjectured that the Heusler structure is stabilized because the Fermi surface barely touches the (110) Brillouin-zone boundary.[1] Recently it was suggested that a band Jahn–Teller effect accompanies the martensitic transformation and the model was confirmed by polarized neutron scattering experiments, where the transfer of magnetic moment from Mn to Ni was found in the martensitic phase.[8,9] Thus the magnetic and structural properties of Ni_2MnGa are strongly dependent on internal parameters such as interatomic distances, stoichiometry, density of 3*d* electron states, concentration of conduction electrons, and *d*–*d* exchange interaction.[2]

Although it has been a subject of attraction during the last few years, many aspects of the behaviors of Ni_2MnGa are not clearly understood. The relative contributions of internal parameters to property variations of Ni_2MnGa based alloys are not sufficiently clarified. Because of the band character of the magnetism, the magnetic characteristics of Heusler alloys are determined by the density of *d*-states at the Fermi level and by the exchange splitting parameter, and depend on the material's structure and composition. Therefore, in most cases of the Ni or Mn subsystem doped alloys, several parameters are varied.

This work was undertaken to study the structural and magnetic properties of the Ni_2MnGa system by the substitution of Mn by magnetic Co and nonmagnetic Cu. The system has been studied with respect to temperature and composition by XRD and magnetization measurements.

EXPERIMENTAL PROCEDURE

5–7 gm of stoichiometric polycrystalline ingots of $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu; $0.0\leqslant x\leqslant 0.25$) were prepared by conventional arc melting in an argon atmosphere using high purity Ni, Mn, Co, Cu, and Ga. The weight loss after melting was found to be less than 0.3 percent. For homogenization, the samples were annealed in vacuum for 72 hours at 900 °C, and slowly cooled down to room temperature.

X-ray diffraction measurements were conducted at room temperature for phase identification and lattice constant determination. The measurements were done on a GBC MMA (Mini Materials Analyzer) x-ray diffractometer that used Cu–K alpha radiation and Bragg–Brentano geometry.

The magnetization measurements were performed on a superconducting quantum interference device (SQUID) made by Quantum Design, Inc. The measurements were performed in a temperature range of 5–400 K and magnetic field of up to 55 kOe.

[a]Author to whom correspondence should be addressed; electronic mail: mkhan@siu.edu

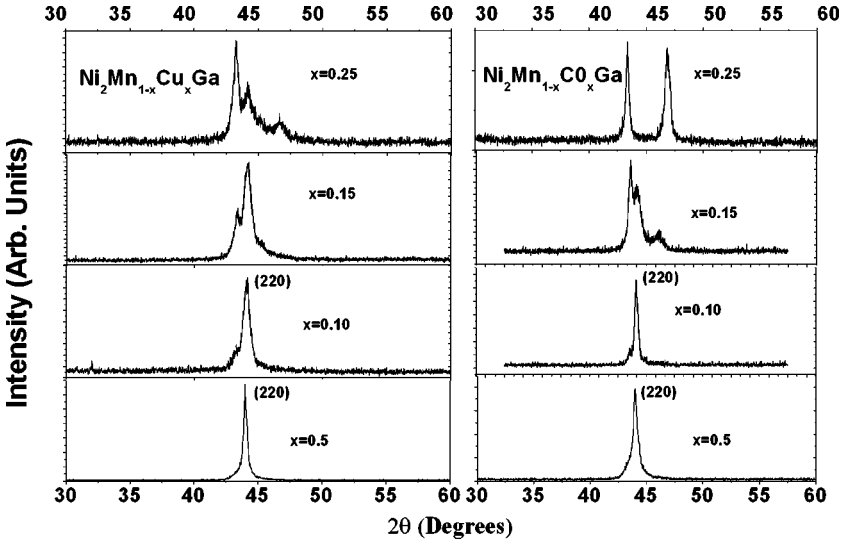

FIG. 1. X-ray powder diffraction patterns of $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu) system with $x=0.05$, 0.10, 0.15, and 0.25, at room temperature.

RESULTS AND DISCUSSION

The (220) peak of the powder x-ray diffraction patterns (XRD) of $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu; $x=0.05$, 0.10, 15, 0.25) system at room temperature are shown in Fig. 1. Both the cobalt and the copper doped systems with $0.00 \leqslant x \leqslant 0.10$ possess the $L2_1$ Heusler structure at room temperature. For the cobalt doped system, a distortion in the peak appears at $x=0.15$ and the peak splits into two for $x=0.25$. There is an apparent similarity between the copper system with $x=0.25$ and the cobalt system with $x=0.15$. The splitting of the XRD peaks could be due to the existence of multiple phases in the $Ni_2Mn_{1-x}M_xGa$ system (M=Co, Cu) for $x>0.10$. Another possibility could be that the systems with $x>0.10$ do not possess the $L2_1$ structure at room temperature. The second reason is more sensible as from the magnetization versus temperature measurements (Figs. 2 and 3) no second phase is observed to be present in the system.

Figure 2 shows the magnetization versus temperature, M(T), curves of the system $Ni_2Mn_{1-x}Co_xGa$ ($x=0.00$, 0.05, 0.08, 0.1, 0.12, 0.15, and 0.25). A gradual increase of both T_M and T_C is observed with increasing Co concentration. For $x=0.15$, the value of T_M is 293 K, which is very close to room temperature. Therefore, the distortion of the XRD peak of the $Ni_2Mn_{1-x}Co_xGa$ system with $x=0.15$ (see Fig. 1) could be due to the fact that the system is in the early stage of the martensitic phase. For $x=0.25$ we do not see any martensitic transformation in the magnetization versus temperature

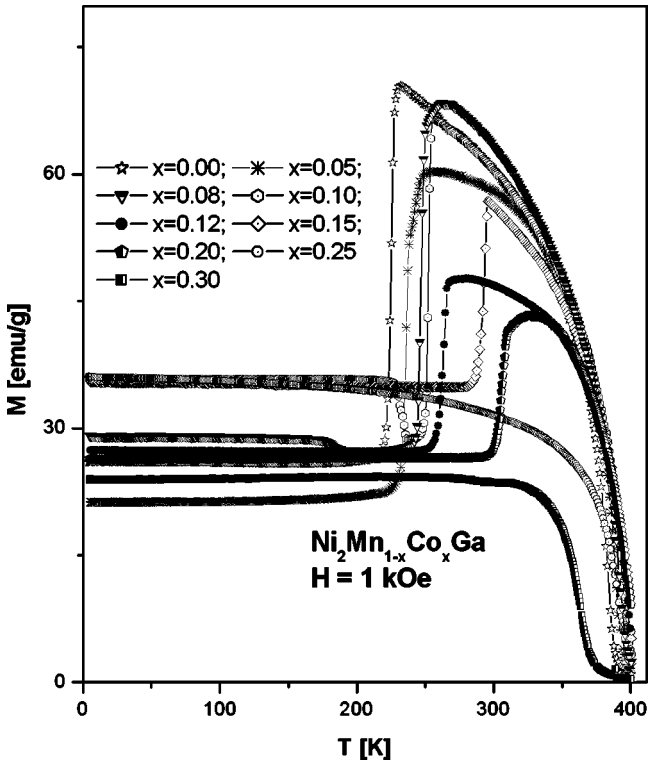

FIG. 2. The temperature variation of magnetization M(T) of $Ni_2Mn_{1-x}Co_xGa$ obtained at a magnetic field of 1 kOe.

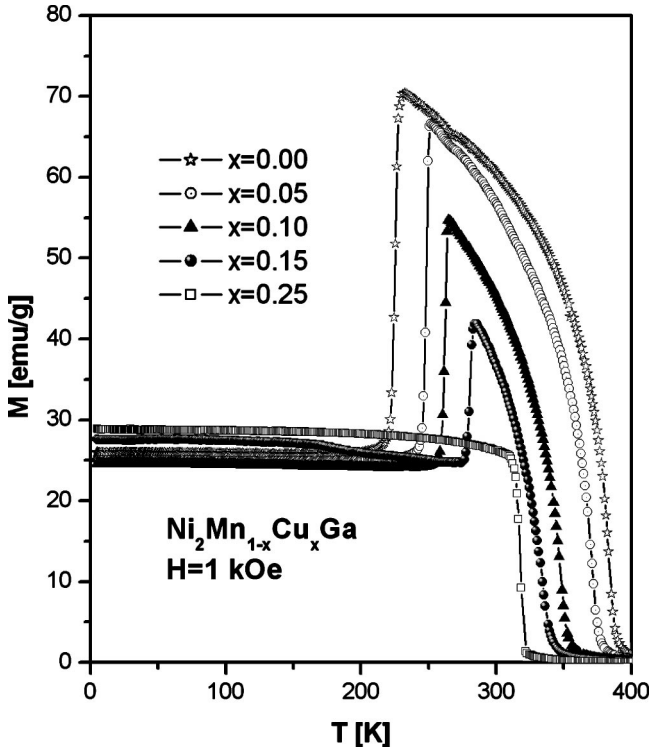

FIG. 3. The temperature variation of magnetization M(T) of $Ni_2Mn_{1-x}Cu_xGa$ obtained at magnetic field of 1 kOe.

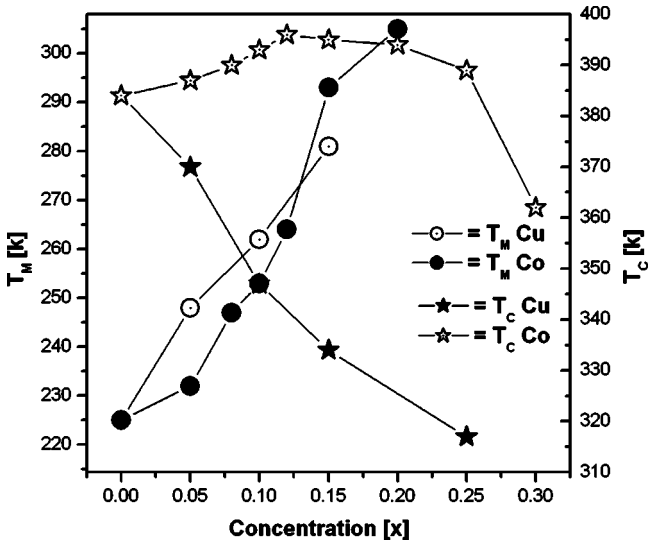

FIG. 4. (T-x) -phase diagram of $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu) obtained from M(T).

curve and splitting of the (220) peak have been observed for this sample. From neutron powder diffraction measurements of Ni_2MnGa the splitting of the peaks has been observed in the martensitic phase.[11] In light of this information and our observations we suggest that the $Ni_2Mn_{1-x}Co_xGa$ system with $x=0.25$ is in the martensitic phase at room temperature. The M(T) curves of the $Ni_2Mn_{1-x}Cu_xGa$ ($x=0.00$, 0.05, 0.10, 0.15, and 0.25) system are shown in Fig. 3. Similar to $Ni_2Mn_{1-x}Co_xGa$ systems, with increasing Cu concentration, T_M increases gradually where as T_C is observed to decrease, and at some critical concentration $(0.15<x<0.25)$, T_M and T_C coincide with each other.

Substitution of Co on the Mn sites in $Ni_2Mn_{1-x}Co_xGa$ results in an increase of T_M (see Fig. 4). In earlier literature,[6,10] it has been suggested that T_M has a proportional relation with the electron concentration, e/a. Since Co has more d electrons than Mn, the substitution of Co on the Mn sites results in an increase of e/a in the $Ni_2Mn_{1-x}Co_xGa$ system, and hence, the increase of T_M with increasing Co concentration in $Ni_2Mn_{1-x}Co_xGa$ is consistent with previous predictions. The effect of increasing e/a on T_M is also clear from the copper doped system. Substituting 5 percent of Co for Mn results in a T_M of 232 K, where as substitution of 5 percent Cu gives a T_M value of 248 K. This makes sense according to the suggested dependence of T_M on e/a, as Cu has more d electrons than Co. The increase of the Curie temperature could be due to the enhancement of the exchange interactions of the system due to the addition of ferromagnetic Co. In the Cu doped system, the decrease of T_C could be due to the fact that Cu is nonmagnetic, and therefore it reduces the exchange interactions of the system.

CONCLUSION

The results of these experimental studies suggest that the $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu) system possesses pure Heusler $L2_1$ structure at room temperature for $x<0.15$. For $x>0.15$ the system is in the early state of the martensitic phase at room temperature. The results also establish the general tendency of both martensitic transition temperature, T_M, and Curie temperature, T_C, to increase with increasing Co concentration in the $Ni_2Mn_{1-x}Co_xGa$ system. Increasing Cu concentration in the $Ni_2Mn_{1-x}Cu_xGa$ system results in an increase of T_M and decrease of T_C. The martensitic transition has been observed in the $Ni_2Mn_{1-x}M_xGa$ (M=Co, Cu) alloys for $0<x<0.25$. The increase of T_M is a possible consequence of its dependence on effective electron concentration, e/a.

ACKNOWLEDGMENT

This work was supported by the Consortium for Advanced Radiation Sources, University of Chicago.

[1] P. J. Webster, K. R. A. Ziebeck, S. L. Town, and M. S. Peak, Philos. Mag. B **49**, 295 (1984).
[2] A. N. Vasil'ev, A. D. Bozhko, V. V. Khovailo, I. E. Dikshtein, V. G. Shavrov, V. D. Buchelnikov, M. Matsumoto, S. Suzuki, T. Takagi, and J. Tani, Phys. Rev. B **59**, 1113 (1999).
[3] M. Matsumoto, T. Takagi, J. Tani, T. Kanomata, N. Muramatsu, and A. N. Vasil'ev, Mater. Sci. Eng., A **273-275**, 326 (1999).
[4] A. N. Vasil'ev, E. I. Estrin, V. V. Khovailo, A. D. Bozhko, R. A. Ischuk, M. Matsumoto, T. Takagi, and J. Tani, Int. J. Appl. Electromagn. Mech. **12**, 35 (2000)
[5] J. Kubler, A. R. Williams, and C. C. Sommers, Phys. Rev. B **28**, 1745 (1983).
[6] Z. H. Liu, M. Zhang, W. Q. Wang, W. H. Wang, J. L. Chen, G. H. Wu, F. B. Meng, H. Y. Liu, B. D. Liu, J. P. Qu, and Y. X. Li, J. Appl. Phys. **92**, 5006 (2002).
[7] T. Kanomata, K. Shirakawa, and T. Kaneko, J. Magn. Magn. Mater. **65**, 76 (1987).
[8] V. V. Khovailo, T. Takagi, J. Tani, R. Z. Levitin, A. A. Cherechukin, M. Matsumoto, and R. Note, Phys. Rev. B **65**, 092410 (2002).
[9] P. J. Brown, A. Y Bargawi, J. Crangle, K.-U. Neumann, and K. R. A Ziebeck, J. Phys.: Condens. Matter **11**, 4715 (1999).
[10] V. A. Chernenko, Scr. Mater. **40**, 523 (1999).
[11] P. J. Brown, J. Crangle, T. Kanomata, M. Matsumoto, K.-U. Neumann, B. Ouladdial, and K. R. A. Zeibeck, J. Phys.: Condens. Matter **14**, 10159 (2002)