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S G. Min
University of New Orleans

L Malkinski
University of New Orleans

Y D. Zhang

S C. Yu

K W. Lee

See next page for additional authors

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S. G. Min,[1] Y. D. Zhang,[2] L. Malkinski,[1] S. C. Yu,[2,a)] K. W. Lee,[3] and Y. C. Kim[4]
[1]*Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148, USA*
[2]*Department of Physics and BK21 Physics Program, Chungbuk National University, Cheongju 361-763, Republic of Korea*
[3]*Industrial Consulting Team, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea*
[4]*Eng., Korea Institute of Science and Technology, Seoul 130-650, Republic of Korea*

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The magnetization behaviors have been analyzed for $Ni_{54}Mn_{21-x}V_xGa_{25}$ $(x=0,2,4)$ alloys which were prepared by conventional arc melting method in argon atmosphere. The Curie temperature T_C was found to be 325, 300, and 265 K and the austenitic transition temperature T_A on heating was found to be 315, 217, and 124 K for $x=0$, 2, and 4, respectively. The magnetic characteristics were performed with a Quantum Design superconducting quantum interference device magnetometer in the field of up to 20 kOe. A large magnetic entropy change ΔS_M, which is calculated from H versus M curves associated with the ferromagnetic-paramagnetic transitions, has been observed. The maximum ΔS_M for an applied field of 2.0 T is 2.49, 1.92, and 1.81 J/kg K for $x=0$, 2, and 4, respectively. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3072819]

I. INTRODUCTION

Temperature change of magnetic materials, associated with an external magnetic field change in an adiabatic process, is defined as the magnetocaloric effect (MCE). The thermal effect was discovered in 1881 by Warburg[1] when he applied varying magnetic field to metal iron. Debye[2] and Giauque[3] explained the nature of MCE later and suggested achieving an ultralow temperature by adiabatic demagnetization cooling. MCE is intrinsic to magnetic solids and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change in the magnetic field. It can be measured and/or calculated as the adiabatic temperature change $\Delta T_{ad}(T,\Delta H)$, or as the isothermal magnetic entropy change $\Delta S_M(T,\Delta H)$.[4–6] The MCE is a function of both temperature T and the magnetic field change ΔH and is usually recorded as a function of temperature at a constant ΔH. Recently, a large magnetic entropy change has been found and intensively studied in intermetallic compounds, due to the possibility of using these materials as active magnetic refrigerants in the magnetic refrigeration technology.[7–9] There are two key requirements for a magnetic material to possess a large MCE. One is a large enough spontaneous magnetization which belongs to a class of heavy rare-earth metals, for example, Gd metal, and the other is a sharp drop in magnetization with increasing temperature, associated with ferromagnetic-paramagnetic transitions at the Curie temperature. The observation of a shape memory effect and superelasticity in ferromagnetic Heusler alloys Ni–Mn–Ga has generated considerable interest among these materials.[10–13]

Ni–Mn–Ga alloy is known to undergo a transition from the martensitic to austenitic structure on heating and a reverse process on cooling, accompanying a magnetization jump.[14] Recently, large field-induced strains in Ni–Mn–Ga alloys have also been observed near the structural transition.[13] The simultaneously changed structural and magnetic properties at the transition are expected to influence strongly the MCE of the alloys. In our article, magnetic and magnetocaloric properties of $Ni_{54}Mn_{21-x}V_xGa_{25}$ $(x=0,2,4)$ compounds were investigated.

II. EXPERIMENTS

The $Ni_{54}Mn_{21-x}V_xGa_{25}$ $(x=0,2,4)$ samples were prepared by the conventional arc melting method in argon atmosphere. For homogeneity of samples, ingot was melted several times. Then, the heat treatment was carried out at 1100 K in a sealed quartz tube for 9 days and quenched in ice water. The samples were examined by the x-ray diffraction and showed the single phase structure. The magnetic characteristics were performed with a Quantum Design superconducting quantum interference device (MPMS mode) magnetometer in the fields of up to 20 kOe. The magnetic entropy change is calculated by the isothermal magnetization measurements with a sensitivity of 10^{-8} emu.

III. RESULTS AND DISCUSSION

According to the thermodynamic theory, the magnetic entropy change caused by the variation in the external magnetic field from 0 to H_{max} is given by

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial S}{\partial H}\right)_T dH. \quad (1)$$

From the Maxwell thermodynamic relationship

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T, \quad (2)$$

Eq. (1) can be rewritten as follows:

a)Electronic mail: scyu@chungbuk.ac.kr.

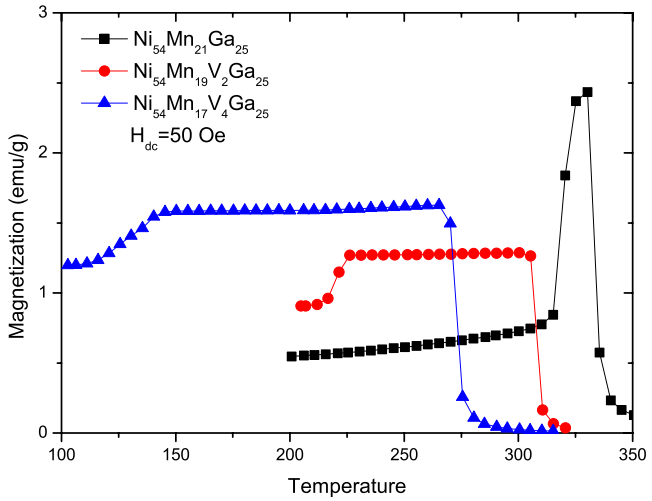

FIG. 1. (Color online) Temperature dependence of the magnetization measured at 50 Oe for $Ni_{54}Mn_{21-x}V_xGa_{25}$ ($x=0,2,4$).

$$\Delta S_M = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right) dH. \tag{3}$$

Numerical evaluation of the magnetic entropy change was carried out from formula (3) using isothermal magnetization measurements at small discrete field and temperature intervals. ΔS_M can be computed approximately from Eq. (3) by

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{M_{i+1} - T_i} \Delta H. \tag{4}$$

Thus, the magnetic entropy changes associated with applied field variations can be calculated from Eq. (4).

The adiabatic temperature change at an arbitrary chosen temperature T_0 can be roughly expressed as[15]

$$\Delta T_{\text{ad}} = -\Delta S_M(T_0,H)\frac{T_0}{C_p(T_0,H)}. \tag{5}$$

Ni_2MnGa belongs to a family of intermetallic compounds known as ternary Heusler alloys. In Heusler alloys Ni_2MnGa with $L21$ structure, the increased nearest-neighbor distances of the Mn atoms compared with pure Mn lead to a positive exchange integral and hence to ferromagnetism. Neutron diffraction experiments performed by Webster *et al.*[16] confirmed the ordered $L21$ structure in Ni_2MnGa single crystal and measured a magnetic moment of about $4.17\mu_B$ for manganese atoms with a small moment of $0.3\mu_B$ associated with the Ni atoms. Ferromagnetic Heusler alloys Ni–Mn–Ga are known to undergo a transition from the tetragonal martensitic to cubic austenitic structure on heating and a reverse process on cooling. Figure 1 shows the temperature dependence of low-field magnetization in the heating process for the $Ni_{54}Mn_{21-x}V_xGa_{25}$ ($x=0,2,4$) compounds. Sharp changes in the magnetization at the austenitic-martensitic and magnetic transition temperatures are observed. The austenitic-martensitic transition temperature T_A was found to be 315, 217, and 124 K and the Curie temperature T_C was found to be 325, 300, and 265 K for $x=0$, 2, and 4 of $Ni_{54}Mn_{21-x}V_xGa_{25}$, respectively. With an increase in the concentration of V for $Ni_{54}Mn_{21-x}V_xGa_x$ systems, the Curie temperature and austenitic transition temperature decrease due to the dilution of the magnetic subsystem.[17]

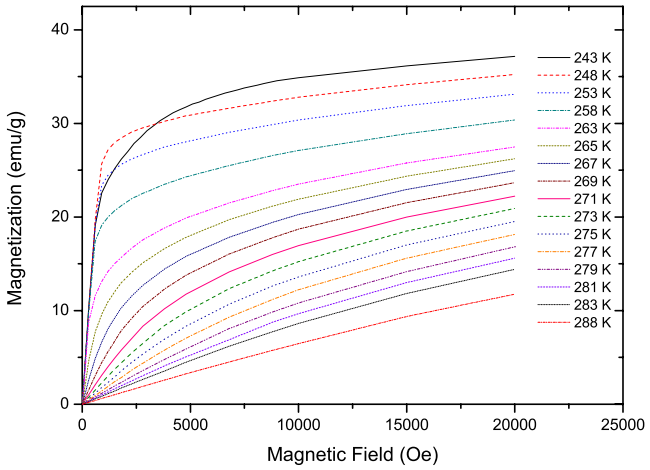

FIG. 2. (Color online) Isothermal magnetization curves in the vicinity of the Curie temperature for the $Ni_{54}Mn_{17}V_4Ga_{25}$.

In Fig. 2, we show the isothermal magnetization versus applied field at various temperatures between 243 and 288 K for the $Ni_{54}Mn_{17}V_4Ga_{25}$ compound. For the measurements around the Curie temperature, the temperature interval is as small as 2 and 5 K. Albertini *et al.*[18] investigated Ni_2MnGa polycrystalline and demonstrated that while the structural transition changes from tetragonal martensite to cubic austenite occur, the dependency of magnetization on applied changes strongly. According to them, the elastic energy stored by martensite gives rise to the magnetic anisotropy, which dominates the magnetization process. As a result, the magnetization of martensite at low temperature is harder to saturate than that of high temperature austenite and the saturated magnetization of the martensite is higher than that of the austenite, as the isothermal curves at 243 and 248 K

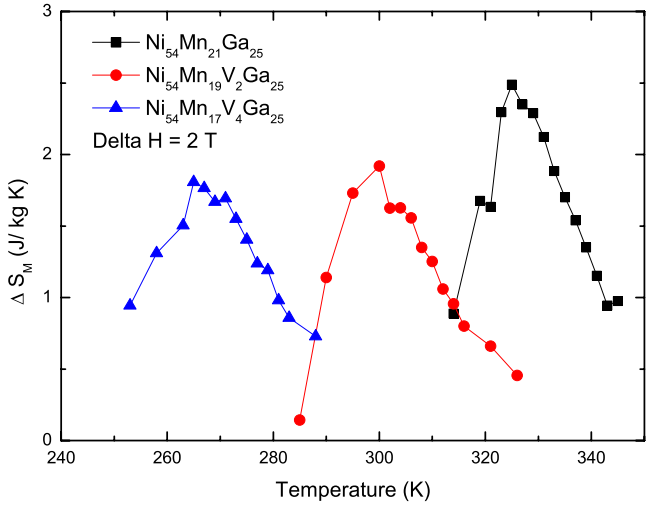

FIG. 3. (Color online) Temperature dependence of magnetic entropy change obtained under a field change from 0 to 2.0 T for $x=0,2,4$ of $Ni_{54}Mn_{21-x}V_xGa_{25}$ compounds.

show in Fig. 2. In evaluating the magnetocaloric properties of the $Ni_{54}Mn_{21-x}V_xGa_{25}$ $(x=0,2,4)$ samples, the magnetic entropy change, a function of temperature and magnetic field, produced by variation in the magnetic field from 0 to H_{max} is calculated through Eq. (4). ΔS_M versus T for the samples was plotted in Fig. 3. As can be seen in Fig. 3, with a magnetic field varying from 0 to 20 kOe, the magnetic entropy change ΔS_M reaches maximum values of about 2.49, 1.92, and 1.81 J/kg K for $x=0$, 2, and 4 at 325, 300, and 265 K, respectively. With increasing V content, the maximum magnetic entropy decreased due to substitution of magnetic Mn ions by nonmagnetic V ions.

IV. CONCLUSIONS

The magnetic properties and magnetocaloric properties of $Ni_{54}Mn_{21-x}V_xGa_{25}$ $(x=0,2,4)$ compounds were investigated. The austenitic-martensitic transition temperature and the Curie temperature decreased with increasing V concentration, and the maximum magnetic entropy change appears at about the Curie temperature. The magnetic entropy change reaches maximum values of about 2.49, 1.92, and 1.81 J/kg K for $x=0,2,4$ of $Ni_{54}Mn_{21-x}V_xGa_{25}$. In comparison with pure Gd metal,[19] the maximum magnetic entropy change is very small, but these samples are very cheap and their Curie temperature can be easily adjusted by tuning the Ni/Mn ratio or V concentration.

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