Structure and magnetism of NiFeMnGaxSn1-x (x=0, 0.25, 0.5, 0.75, 1.00) Heusler compounds

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ABSTRACT
The crystal structure and magnetic properties of NiFeMnGa\textsubscript{x}Sn\textsubscript{1-x} (x = 0, 0.25, 0.50, 0.75, 1.00) Heusler compounds have been investigated experimentally and theoretically. The computational results suggest that NiFeMnGa\textsubscript{0.75}Sn\textsubscript{0.25} is nearly half-metallic with a spin polarization P of 87%. The bulk samples prepared using arc-melting and annealing exhibit a high degree of Y-type order. All the investigated samples show ferromagnetic spin order with the Curie temperatures ranging from 284 K for NiFeMnGa to 408 K for NiFeMnSn. The intermediate composition NiFeMnGa\textsubscript{0.75}Sn\textsubscript{0.25}, which is predicted to be nearly half metallic, has a saturation magnetization of 66.50 emu/g and Curie temperature of 326 K. These results indicate that the NiFeMnGa\textsubscript{0.75}Sn\textsubscript{0.25} alloy has potential for spin-transport-based devices.

I. INTRODUCTION

Magnetic materials exhibiting high transport-spin-polarization at the Fermi level have been actively investigated for their applications in spin-transport-based electronic devices, where the information storage, processing, and manipulation are achieved by electronic spins.\textsuperscript{1} An ideal candidate for spintronic applications is a room-temperature half-metal, a material that behaves as an insulator for one spin channel and a conductor for the opposite spin channel.\textsuperscript{1–4} Ideally, half-metals are capable of producing fully (100%) spin-polarized currents, which maximize the efficiency of spintronic devices including spin-transfer torque (STT) magnetoresistive random-access memories (MRAM).\textsuperscript{5} Several materials from the Heusler family of compounds exhibiting half-metallic band structures have been theoretically predicted and a few of them are realized experimentally.\textsuperscript{5–17} For example, the half-metallic properties in NiMnSb and Co\textsubscript{2}MnSi are confirmed using spin-polarized positron-annihilation and surface sensitive ultraviolet photoemission spectroscopy, respectively.\textsuperscript{18–20} Further, the high values of transport-spin-polarization have been reported in CoFeCrAl epitaxial thin films and Mn\textsubscript{2}CrGa ribbons using point-contact Andreev reflection spectroscopy.\textsuperscript{21,22}

The NiFeMnGa and NiFeMnSn compounds belong to the class of quaternary Heusler compounds with the cubic Y-type crystal structure (F\textsubscript{4}3m space group). Recently, these materials have been reported to exhibit nearly half-metallic electronic band structures.\textsuperscript{23,24} Although NiFeMnGa has been predicted to be half-metallic, its Curie temperature is too low for device applications.\textsuperscript{23} On the other hand, NiFeMnSn is not fully half-metallic but its Curie temperature (\textit{T}_\text{c} = 405 K) is relatively high.\textsuperscript{24} However, our first-principle calculations indicate that NiFeMnGa does not show half-metallic band structure but the intermediate composition, namely, NiFeMnGa\textsubscript{0.75}Sn\textsubscript{0.25} exhibits a higher value of spin polarization as compared to that of both NiFeMnGa and NiFeMnSn. Here, we report the results of our first-principle calculations on a series of compounds NiFeMnGa\textsubscript{x}Sn\textsubscript{1-x} (x = 0, 0.25, 0.50, 0.75, 1.00) and compare the predicted structural and magnetic properties with that of NiFeMnGa\textsubscript{x}Sn\textsubscript{1-x} compounds synthesized using arc-melting and
annealing. Although our main focus is on NiFeMnGa$_{0.75}$Sn$_{0.25}$, the composition predicted to show high spin polarization, the experimental data collected on samples with other compositions are also discussed.

II. METHODS

A. Computational methods

We performed density functional calculations of bulk NiFeMnGa$_x$Sn$_{1-x}$ (x = 0, 0.25, 0.50, 0.75, 1.00), using the projector augmented-wave method (PAW),

 implemented in the Vienna \emph{ab initio} simulation package (VASP)\cite{vasp},

 within the generalized-gradient approximation (GGA).\cite{gga} The integration method\cite{integration} with a 0.05 eV width of smearing was used, along with the plane-wave cut-off energy of 500 eV and energy convergence criteria of 10$^{-7}$ meV for atomic relaxation (resulting in the Hellmann–Feynman forces being less than 0.005 eV/Å), and 10$^{-5}$ meV for the total energy and electronic structure calculations. A k-point mesh of 12$\times$12$\times$12 was used for the Brillouin-zone integration. All calculations were performed for 16-atom cubic super cell with periodic boundary condition imposed. For all ground state calculations, the lattice geometry was fully optimized to obtain equilibrium structures. Some of the results were obtained using the MedeA$^\text{®}$ software environment\cite{medea} and the Extreme Science and Engineering Discovery Environment (XSEDE) resources located at the Pittsburgh Supercomputing Center (PSC).\cite{xsede} We used MedeA software to generate and visualize the initial crystal structures.

B. Experimental methods

We prepared a series of compounds, NiFeMnGa$_x$Sn$_{1-x}$ (x = 0, 0.25, 0.5, 0.75, 1.00), in the form of bulk ingots using arc melting and annealing. First, small pieces of Ni, Fe, Mn, Ga and Sn with the proper weight ratio were cut from commercially available pellets and melted on a water-cooled Cu hearth of an arc-melting furnace in a highly pure argon environment. The arc-melted alloy ingots were annealed at 800°C for 15 hours under a flow of nitrogen gas followed by rapid quenching in liquid nitrogen. Each sample was ground into a fine powder for structural analysis. The crystal structure of the powder samples were investigated using powder x-ray diffraction (XRD) in a Rigaku MiniFlex diffractometer with a copper Ka radiation. The XRD patterns were analyzed by Rietveld method using the FullProof suite software. Magnetic properties were investigated using a Quantum Design VersaLab vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSION

A. Computational results

Figures 1(a) and 1(b) respectively show the atom-projected density of states (DOS) for NiFeMnGa (a = 5.75 Å) and NiFeMnSn (a = 6.03 Å), calculated at the optimized lattice constants. Although, both compounds exhibit high values of spin polarizations, neither of them is perfectly half-metallic. The calculated values of P are 75% and 56% for NiFeMnGa and NiFeMnSn, respectively, where $P = \frac{N_F-E_F}{N_F+E_F}$, and $N_{\uparrow\downarrow}(E_F)$ are the spin-dependent density of states at the Fermi level, $E_F$. Our calculated values of $P$ are smaller than the values, $P$ = 100% for NiFeMnGa and $P$ = 76% for NiFeMnSn, reported in Refs. 23 and 24, respectively. This discrepancy can be attributed to the energy smearing schemes used in electronic structure calculations.

On the other hand, the total DOS near the Fermi level for the intermediate compositions $x$ = 0.25, 0.50 and 0.75 in NiFeMnGa$_{0.75}$Sn$_{0.25}$ (not shown) also have similar profile but the value of P exhibits strong dependence on x. As shown in Fig. 2(a), the value of $P$ increases from 56% for $x$ = 0 to 87% for $x$ = 0.75, and then decreases for further increase in x reaching 75% for $x$ = 1.00. Figure 2(a) also shows elemental composition dependence of the total magnetic moment and lattice parameter. As shown in the inset of Fig. 2(a), the lattice constant $a$ decreases linearly with increasing x from 6.03 Å for NiFeMnSn to 5.75 Å for NiFeMnGa. Further, the total magnetic moment per 16-atom cell also decreases linearly from 20.08 $\mu_B$ (5.02 $\mu_B$/f.u.) to 16.09 $\mu_B$ (4.02 $\mu_B$/f.u.) as x increases from 0 to 1 in NiFeMnGa$_x$Sn$_{1-x}$. The decrease in the total magnetic moment is associated with the decrease of the local magnetic moments on Fe and Mn atoms, as illustrated in Fig. 2(b). The calculated lattice constants are close to the values obtained from Rietveld analysis but the total magnetic moments are slightly larger than the experimental values, as discussed below.
B. Experimental results

Figure 3(a) shows the powder XRD patterns for the nitrogen-annealed NiFeMnGa$_{x}$Sn$_{1-x}$ ($x = 0, 0.25, 0.50, 0.75, 1.00$) samples measured at room temperature. The nitrogen annealing has substantially improved the crystalline quality of the samples as noted by the increase of the relative intensities of characteristic peaks. The diffraction patterns were compared with the patterns simulated using the FullProof suite software.$^{31,32}$ As an example, the simulated and experimental XRD patterns of the NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound are shown in Fig. 3(b). The simulation was done assuming the LiMgPdSn-type Heusler structure (Y-type with space group $F\bar{4}3m$), where $4a \ ((0, 0, 0))$, $4b \ ((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}))$, $4c \ ((\frac{1}{2}, \frac{1}{2}, 0))$, and $4d \ ((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}))$ lattice sites are occupied by Sn/Ga, Mn, Fe, and Ni, respectively. All the simulated patterns very closely match the corresponding experimental patterns without considering any elemental or alloy impurities. The Bragg R-factor and RF-factor (R-indices) obtained from the fits are 4.51 and 5.61, respectively. However, a $L2_1$ type disorder due to mixing of Fe and Ni atoms cannot be ruled out because it is very difficult to distinguish between the Y-type and $L2_1$ orders using only Rietveld analysis. The lattice constants determined from the Rietveld analysis are 5.733, 6.028, 5.581, 5.992, and 6.064 Å for $x = 0, 0.25, 0.50, 0.75$, and 1.00 in NiFeMnGa$_{x}$Sn$_{1-x}$, respectively. As shown in Fig. 3(a), the $(111)$ and $(200)$ superlattice peaks are absent in the patterns of the NiFeMnSn and NiFeMnGa$_{0.75}$Sn$_{0.25}$ compounds. Although the intensity of the superlattice peaks in NiFeMnGa is very small because of the identical scattering amplitudes of the constituent elements, the possibility of site disorder cannot be ruled out.$^{23,33}$ The superlattice peaks become stronger with increasing Sn concentration in NiFeMnGa$_{x}$Sn$_{1-x}$. The apparent shift of the intensity peaks towards higher diffraction angles with increasing Ga content is due to lattice contraction caused by a partial replacement of Sn atoms with Ga atoms having smaller atomic sizes.

Figure 4(a) shows the isothermal magnetization $M(H)$ curves for the NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound recorded at 100 K and the right inset plots the saturation magnetization as a function of $x$ in NiFeMnGa$_{x}$Sn$_{1-x}$. The $M(H)$ curves have very small coercivities (less than 30 Oe) and the magnetizations saturate at relatively low magnetic fields, showing soft magnetic behavior. As shown in the right inset of Fig. 4(a), the saturation magnetization ($M_s$) is sensitive to the value of $x$, where the $M_s$ decreases almost linearly with the increase in $x$ from 76.15 emu/g (3.93 $\mu_B$/f.u.) for NiFeMnSn to 61.6 emu/g (2.64 $\mu_B$/f.u.) for NiFeMnGa. These values of magnetizations are smaller than the values predicted by our first-principle calculations and the Slater Pauling rule for the half-metallic state of these compounds. One of the possible reasons for the lower values of saturation magnetizations in our samples is the site disorder. As mentioned in the structural analysis above, Heusler compounds are prone to the site disorder and it is difficult to identify the type of

![FIG. 2](image)

**FIG. 2.** (a) Calculated spin polarization (black squares), total magnetic moment per 16-atom cell (blue circles), and lattice constant (inset) of NiFeMnGa$_{x}$Sn$_{1-x}$ ($x = 0, 0.25, 0.50, 0.75, 1.00$). (b) Calculated atom-resolved magnetic moment of NiFeMnGa$_{x}$Sn$_{1-x}$ ($x = 0, 0.25, 0.50, 0.75, 1.00$).

![FIG. 3](image)

**FIG. 3.** (a) Powder x-ray diffraction patterns for nitrogen-annealed NiFeMnGa$_{x}$Sn$_{1-x}$ ($x = 0, 0.25, 0.50, 0.75, 1.00$) samples. (b) Rietveld refinement plot for NiFeMnGa$_{0.75}$Sn$_{0.25}$ sample with the corresponding experimental data (Inset shows a cubic Y-type crystal structure of NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound).
IV. CONCLUSIONS

Figure 4(b) shows the thermomagnetic curve $M(T)$ for the NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound recorded at 1 kOe, and the lower inset plots the Curie temperature as a function of $x$ in NiFeMnGa$_{x}$Sn$_{1-x}$ compounds. The $M(T)$ curves for all these samples show similar behaviors, where the magnetizations gradually decrease with increasing temperature undergong magnetic phase transitions at their Curie temperatures. The magnetic transitions near the Curie temperatures are sharp, similar to that of ferromagnetic materials. As shown in the lower inset of Fig. 4(b), the $T_c$ systematically decreases with increasing $x$ in NiFeMnGa$_{x}$Sn$_{1-x}$ from 408 K for $x = 0$ to 284 K for $x = 1$. The values of Curie temperatures were determined from the lowest points in the corresponding $dM/dT$ curves. As an example, the $dM/dT$ versus $T$ curve for the NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound with $T_c = 326$ K is displayed in the upper inset of Fig. 4(b).

IV. CONCLUSIONS

We have conducted a combined computational and experimental investigation of the crystal structure and magnetic properties of bulk NiFeMnGa$_{x}$Sn$_{1-x}$ ($x = 0, 0.25, 0.5, 0.75, 1.00$) compounds. Computational results suggest that the NiFeMnGa$_{0.75}$Sn$_{0.25}$ compound is nearly half-metallic with a spin polarization $P$ of 87%. All the investigated samples have cubic Heusler structure without any secondary phases but only the Sn-rich samples show superlattice peaks expected for the ordered $\gamma$-structure. Both the saturation magnetization and Curie temperature are sensitive to the elemental compositions, where both the $M_S$ and $T_c$ are higher for the Sn-rich samples. The predicted composition NiFeMnGa$_{0.75}$Sn$_{0.25}$, which is predicted to be nearly half metallic, has a saturation magnetization of 66.50 emu/g and Curie temperature of 326 K. These results are promising and further investigation into the thin films of NiFeMnGa$_{0.75}$Sn$_{0.25}$ is required for spintronic device applications.

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