Magnetism and electron transport of MnyGa (1 < y < 2) nanostructures

Y. Huh
University of Nebraska-Lincoln, yung.huh@sdstate.edu

Parashu Kharel
University of Nebraska at Lincoln, pkharel2@unl.edu

V.R. Shah
University of Nebraska-Lincoln

XINGZHONG LI
Nebraska Center for Materials and Nanoscience, xli2@unl.edu

Ralph Skomski
University of Nebraska at Lincoln, rskomski2@unl.edu

See next page for additional authors

Follow this and additional works at: http://digitalcommons.unl.edu/physicsskomski

Huh, Y.; Kharel, Parashu; Shah, V.R.; LI, XINGZHONG; Skomski, Ralph; and Sellmyer, David J., "Magnetism and electron transport of MnyGa (1 < y < 2) nanostructures" (2013). Ralph Skomski Publications. Paper 83.
http://digitalcommons.unl.edu/physicsskomski/83

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Ralph Skomski Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
Magnetism and electron transport of Mn$_y$Ga (1 < y < 2) nanostructures

Y. Huh,1,2 P. Kharel,1,3 V. R. Shah,1 X. Z. Li,1 R. Skomski,1,3 and D. J. Sellmyer1,3
1Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, USA
2Department of Physics, South Dakota State University, Brookings, South Dakota 57007, USA
3Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA

(Received 24 April 2013; accepted 13 June 2013; published online 1 July 2013)

Nanostructured Mn$_y$Ga ribbons with varying Mn concentrations including Mn$_{1.2}$Ga, Mn$_{1.4}$Ga, Mn$_{1.6}$Ga, and Mn$_{1.9}$Ga were prepared using arc-melting and melt-spinning followed by a heat treatment. Our experimental investigation of the nanostructured ribbons shows that the material with y = 1.2, 1.4, and 1.6 prefers the tetragonal $L_1_0$ structure and that with y = 1.9 prefers the $D_0_{22}$ structure. We have found a maximum saturation magnetization of 621 emu/cm$^3$ in Mn$_{1.5}$Ga which decreases monotonically to 300 emu/cm$^3$ as y reaches 1.9. Although both the $L_1_0$- and $D_0_{22}$-Mn$_y$Ga samples show a high Curie temperature ($T_C$) well above room temperature, the value of $T_C$ decreases almost linearly from 702 K for Mn$_{1.6}$Ga to 551 K for Mn$_{1.2}$Ga. All the ribbons are metallic between 2 K and 300 K but the Mn$_{1.2}$Ga also shows a resistance minimum near 15 K. The observed magnetic properties of the Mn$_y$Ga ribbons are consistent with the competing ferromagnetic coupling between Mn moments in the regular $L_1_0$-Mn$_y$Ga lattice sites and antiferromagnetic coupling with excess Mn moments occupying Ga sites. 

INTRODUCTION

Magnetic materials having high magnetic anisotropy and Curie temperature well above room temperature have high potential for a range of applications including high-density recording, nonvolatile memory, and permanent-magnet materials.1–3 Most high-anisotropy magnets contain either rare-earth elements or noble metals such as Pt.3 Some of the rare-earth elements used in strong permanent magnets are critical materials and there are serious concerns over the price and supply of these materials.4 Therefore, there have been intense research efforts in identifying and developing novel rare-earth free high-anisotropy magnets. Some of the non-rare-earth-element-based permanent magnet materials of current interest are the manganese-based ferromagnetic materials including MnBi,5,6 MnAl,7 and MnGa.8–10 Among these three magnets, Mn$_y$Ga is particularly interesting because its magnetic properties can be tuned by varying y to fit specific magnetic and magnetoelectronic applications.11,12

Mn$_y$Ga can be synthesized in multiple crystallographic structures including cubic (disordered Cu$_3$Au-type structure), hexagonal ($D_0_{19}$), tetragonal ($L_1_0$), and tetragonal ($D_0_{22}$) structures.13 Theoretically, Mn$_y$Ga in a cubic Heusler ($L_2_1$) structure with half-metallic electronic band structure has also been predicted but there is no experimental evidence to support this prediction to date.14 The most extensively studied phases of Mn$_y$Ga compounds are the tetragonal $L_1_0$ (1 < y < 1.8) and $D_0_{22}$ (2 ≤ y ≤ 3) structures. Theoretically, Mn$_y$Ga compounds in $L_1_0$ and $D_0_{22}$ structures are expected to have anisotropy constant $K_u$ of 26 and 20 Mergs/cm$^3$, magnetization $M_s$ of 845 and 305 emu/cm$^3$, energy product ($BH_{max}$) of 28.2 and 3.67 MGOe, and spin polarization at the Fermi level of 71% and 88%, respectively.15,16 The highest experimental values of $H_c$ and $K_u$ for $L_1_0$-Mn$_y$Ga are reported for $L_1_0$-Mn$_{1.7}$Ga films grown epitaxially on GaAs substrates and are 42.8 kOe and 21.7 Mergs/cm$^3$, respectively.9 Although $L_1_0$-Mn$_y$Ga shows relatively small magnetization for permanent-magnet application, the high values of anisotropy constant and coercivity; and Curie temperature well above room temperature are promising and the material might be used to develop nanocomposite permanent magnets. Therefore, it is important to understand the structural and magnetic properties of $L_1_0$-Mn$_y$Ga compound in nanoparticle or nanoribbon form. Further, the predicted high value of spin polarization (71%) has motivated us to investigate its electrical properties as well. Here, we present our experimental investigation on the structural, magnetic, and electron-transport properties of single phase $L_1_0$-Mn$_y$Ga ($y$ = 1.2, 1.4, and 1.6) nanostructures in the form of ribbons which has not been reported to date. For comparison, we have also included experimental data of the tetragonal $D_0_{22}$-Mn$_{1.9}$Ga sample.

EXPERIMENT

Mn$_y$Ga ($y$ = 1.2, 1.4, 1.6, and 1.9) nanostructured ribbons were prepared using arc-melting, melt-spinning, and annealing. The arc-melting process, which produces Mn$_y$Ga ingots from the respective metal pieces, was carried out on a water-cooled Cu hearth in a highly pure argon environment. The Mn$_y$Ga ingots were then inductively heated in a quartz tube and molten metal was ejected onto the surface of a rotating copper wheel where it rapidly solidified into ribbons. The ribbons are about 1 mm wide and 10 μm thick. The tangential speed of the rotating wheel was kept at 20 m/s for all the samples and the melt-spinning process was carried out in a chamber filled with a suitable pressure of high-purity argon gas. The ribbons were annealed in a tubular vacuum furnace with a base pressure ~10$^{-7}$ Torr at temperatures between...
400 °C and 450 °C. Mn$_{1.2}$Ga ribbons were annealed at 400 °C for 7 h and Mn$_{1.4}$Ga, Mn$_{1.6}$Ga, and Mn$_{1.9}$Ga ribbons were annealed at 450 °C for 50 h to obtain the single-phase tetragonal structure. These annealing times are much shorter than the previously reported time of two to three weeks required for an arc-melted ingot to crystallize into a tetragonal phase. The elemental compositions in the Mn$_y$Ga alloys were estimated from the weights of the starting metal pieces and were later confirmed using energy-dispersive x-ray spectroscopy (EDS) on Joel JSM 840 A. The EDS values were very close to the initially estimated values within an error of 0.1 at. %. The room-temperature structural properties of the samples were studied using x-ray diffraction (XRD) in a Rigaku x-ray diffractometer and their microstructures were investigated using a FEI Tecnai Osiris Transmission Electron Microscope (TEM). A Quantum Design superconducting quantum interference device (SQUID) magnetometer and a Physical Properties Measurement System (PPMS) were used to investigate the magnetic and electron transport properties of the ribbons.

RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns of Mn$_y$Ga (y = 1.2, 1.4, and 1.6) ribbons measured at room temperature. All the diffraction peaks in the XRD patterns are indexed with the expected tetragonal $L1_0$-structure. However, as shown in the inset of Fig. 1(a), Mn$_{1.9}$Ga ribbons annealed at 450 °C for 50 h crystallized in a different structure, the tetragonal $D0_{22}$ structure (c/a = 1.85). All the samples are polycrystalline but very small texture was observed in the ribbons. In order to understand the detailed crystal structure and to quantify the impurity phases, a Rietveld refinement of diffractograms of all the ribbon samples was carried out using the Topas software. We also determined the c and a-axis lattice parameters from the Rietveld refinement of the XRD data (see Table I). Figure 1(b) shows a simulated powder diffraction pattern for tetragonal Mn$_{1.6}$Ga alloy which is plotted with the experimental data. The intensities and 2θ positions of the diffraction peaks in the experimental pattern show a very close match with the simulated pattern indicating that the samples have crystallized in the tetragonal $L1_0$ structure. As all the Bragg reflections are accounted for by the $L1_0$ phase, we have not considered any secondary alloy phases and elemental impurities in the samples for Rietveld refinement. This suggests that the samples are single phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn$_{1.2}$Ga</th>
<th>Mn$_{1.4}$Ga</th>
<th>Mn$_{1.6}$Ga</th>
<th>Mn$_{1.9}$Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>c (Å)</td>
<td>3.720</td>
<td>3.661</td>
<td>3.633</td>
<td>7.239</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.873</td>
<td>3.882</td>
<td>3.893</td>
<td>3.918</td>
</tr>
</tbody>
</table>

FIG. 1. (a) Room-temperature x-ray diffraction patterns of Mn$_{1.2}$Ga, Mn$_{1.4}$Ga, and Mn$_{1.6}$Ga ribbons which are indexed to the tetragonal $L1_0$ structure. The inset shows an XRD pattern of Mn$_{1.9}$Ga ribbon indexed to the tetragonal $D0_{22}$ structure. (b) A simulated powder x-ray diffraction pattern (Rietveld plot) corresponding to the tetragonal-$L1_0$ structure of Mn$_{1.6}$Ga alloy with the experimental data (red line). The difference between the data and the fit is shown in blue color. The inset plots the lattice parameters a and c obtained from the Rietveld analysis of the XRD data as a function of y in Mn$_y$Ga (y = 1.2, 1.4, and 1.6) alloy. (c) $L1_0$-Mn$_y$Ga unit cell.
Mn$_y$Ga. As shown in the inset of Fig. 1(b) and Table I, both the $c$ and $a$-axis lattice constants show a significant change with the change in Mn concentration in Mn$_y$Ga. Although the change in $a$ is small, the $c$-axis lattice parameter substantially decreases (approximately 2.4%) as $y$ increases from 1.2 to 1.6. Such decrease of $c$ with increasing $y$ has also been observed in the bulk and thin film $L1_0$-Mn$_y$Ga alloys.

Although the excess Mn atoms are believed to occupy some of the Ga sites causing a change in the lattice constants, the exact arrangement of these atoms in the $L1_0$ lattice is not known. For Rietveld refinement, we also assumed statistical fractional occupation of Mn atoms at the Ga sites. Figure 1(c) shows the stoichiometric MnGa unit cell in $L1_0$ structure.

In order to determine the average particle size and to understand the microstructure of the ribbons, we have performed dark-field (DF) and high resolution TEM studies of one of the three samples, namely Mn$_{1.6}$Ga. The DFTEM image was taken with incident beam rotating along the peripheral of the selected diffraction rings so that all diffraction rings go through the object aperture. This allowed us to find more bright particles in the DFTEM image. As shown in the DFTEM micrograph (the left panel of Fig. 2), the specimen prepared from the Mn$_{1.6}$Ga ribbon contains nanostructured particles with nonuniform size distribution and with many overlapping particles. The average particle size in the ribbon is about 35 nm $\pm$ 2 nm. The high-resolution TEM image (the right panel of Fig. 2) shows that the particles are single grained or have overlapping grains. The selected area diffraction (SAED) pattern was a ring pattern (not shown) confirming the polycrystalline nature of the sample. The crystal structure and lattice parameters determined from the TEM studies are consistent with the ones found from XRD analysis.

One of the interesting features of the Mn$_y$Ga alloy is its tunable magnetic property. We have found that the magnetic properties including magnetization, coercivity, anisotropy energy, and Curie temperature of $L1_0$-Mn$_y$Ga alloy are very sensitive to the alloy composition. Figure 3(a) shows the field-dependent magnetization of Mn$_y$Ga ribbons measured at room temperature. All the samples show significant coercivities but the magnetizations are not saturated even at 70 kOe. This suggests that Mn$_y$Ga ribbons have relatively large magnetic anisotropy as the polycrystalline samples of high anisotropy magnetic materials typically show such unsaturated M(H) loops. We have measured a high field (H = 70 kOe) magnetization as high as 621 emu/cm$^3$ in Mn$_{1.2}$Ga ribbons which decreases almost linearly to 500 emu/cm$^3$ as $y$ increases from 1.2 to 1.6. These values were calculated using the density (7.3 g/cm$^3$) of a stoichiometric MnGa alloy. The highest magnetization observed in our study (621 emu/cm$^3$) is smaller than the theoretically predicted value (845 emu/cm$^3$) for $L1_0$-MnGa alloy but is the highest experimental value for polycrystalline Mn$_y$Ga compound reported to date. On the other hand, Mn$_{1.9}$Ga ribbon which has $D0_{22}$ structure shows small magnetization of about 300 emu/cm$^3$ but the coercivity is slightly larger and is about 2.5 kOe. However, a high coercivity close to 10 kOe and $M_r/M_s$ ratio more than 70% have been achieved after a magnetic field alignment of the powder samples prepared by a mechanical grinding of the ribbons (Fig. 3(a) inset). These values of magnetization and coercivity are comparable with the previously reported values for epitaxially grown $D0_{22}$-Mn$_2$Ga films.

The decrease of magnetization with increasing $y$ in Mn$_y$Ga ribbons suggests the possibility of having competing ferro- and antiferro-magnetic coupling in our samples. As mentioned above, we believe that the excess Mn atoms in the Mn$_y$Ga ribbons may occupy some of the Ga sites.
sites which couple antiferromagnetically with the Mn atoms in the regular $L_1_0$ lattice. This is consistent with a theoretical prediction that the excess Mn atoms (d) in $L_1_0$-Mn$_{1+d}$Ga occupy some of the Ga sites and couple antiferromagnetically with the rest of the Mn lattice.\textsuperscript{15}

The anisotropy energy $K_u$, one of the most important properties of hard magnetic materials, was calculated using the approach-to-saturation method, where the high-field data were fitted to $M = M_0 \left(1 - A/H^2\right) + \chi H$; $A = 4K_u^2/15M_0^3$. The parameters $M_0$, $A$, and $\chi$ are the spontaneous magnetization, a constant that depends on $K$ and the high field susceptibility, respectively.\textsuperscript{21} As shown in Fig. 3(b), $K_u$ follows the trend of magnetization and decreases from 14 Meqgs/cm$^3$ to 7 Meqgs/cm$^3$ as $y$ increases from 1.2 to 1.6. We note that the observed coercivity in our Mn$_y$Ga ribbons does not scale with the anisotropy energy. Since coercivity is not an intrinsic magnetic property and also depends on the microstructure and texture of a sample, we do not expect the coercivity of the polycrystalline ribbons of a perpendicular anisotropy material to scale with their anisotropy energy.

The temperature dependence of magnetization for Mn$_y$Ga ($y = 1.2, 1.4, 1.6,$ and 1.9) ribbons is shown in Fig. 4. The magnetizations were measured at 1 kOe external field as the temperature increased from 300 K to 800 K. All the Mn$_y$Ga samples show high ferromagnetic moments at room temperature but the magnetizations drastically decrease as the samples pass through their Curie temperatures ($T_c$). As shown in the inset of Fig. 4, all the samples show very high Curie temperatures, well above room temperature. The Curie temperatures of Mn$_y$Ga ribbons show a strong composition dependence and increase almost linearly from 551 K to 702 K as $y$ increases from 1.2 to 1.9. We note that $DO_{22}$-Mn$_y$Ga nanostructures with $y$ greater than 2.5 undergo structural phase transition before the Curie temperature is reached. But, interestingly, the structural and magnetic transitions are decoupled for $DO_{22}$-Mn$_y$Ga with $y \leq 2.1$.\textsuperscript{13} This is true for $L_1_0$-Mn$_y$Ga nanostructures as well and the measured phase-transition temperatures correspond to the real Curie temperatures.

The electrical resistances of Mn$_y$Ga ribbons were measured as a function of temperature between 2 K and 300 K using a four-point-probe method. The data were recorded during cooling from 300 K to 2 K. As shown in Fig. 5, the resistances are normalized to the value at 2 K for better comparison. All the samples are highly conducting and show typical metallic behavior where the resistances increase as temperature increases. The residual resistances are in the range of tens of milliohms (resistivity at 2 K $\approx 2 \times 10^{-5} \Omega$ cm for Mn$_{1.2}$Ga). The low temperature resistances of Mn$_y$Ga samples with $y = 1.4, 1.6,$ and 1.9 are almost constant but the sample with $y = 1.2$ shows a resistance minimum followed by a small upturn below the minimum. Such resistivity minima have also been observed in Mn$_y$Ga films and are attributed to the structural disorder and grain boundary scattering.\textsuperscript{22} The suppression of resistivity minima in samples having higher Mn concentrations may have been caused by their higher residual resistances. The residual resistance ratio (RRR) defined as $R_{300K}/R_{2K}$ is 2.3 for Mn$_{1.2}$Ga which decreases with increasing Mn concentration and reaches 1.7 for Mn$_1$Ga. These values are very close to those reported for high quality epitaxial films grown on GaN (0001) layer using molecular beam epitaxy.\textsuperscript{22} The decrease in the RRR with increasing Mn concentration can be attributed to the structural disorder caused by a partial occupation of some of the Ga sites by the excess Mn atoms.

CONCLUSIONS

In summary, the structural, magnetic, and electron-transport properties of single phase Mn$_y$Ga ($y = 1.2, 1.4, 1.6,$ and 1.9) ribbons prepared by arc melting, melt spinning, and annealing have been investigated. X-ray diffraction showed that the Mn$_y$Ga ribbons with $y = 1.2, 1.4,$ and 1.6 crystallize in the tetragonal $L_1_0$ structure whereas the sample with $y = 1.9$ crystallizes in the tetragonal $DO_{22}$ structure. The magnetic properties of the samples were found to be very sensitive to the elemental composition of Mn$_y$Ga alloy where the magnetization and anisotropy energy decrease and Curie temperature increases with increasing $y$. All the ribbons showed metallic electron transport between 2 K and 300 K but the
Mn$_{1.2}$Ga also showed a resistance minimum near 15 K. The observed magnetic properties are consistent with a ferromagnetic structure in the perfectly ordered $L_1_0$-MnGa lattice plus an antiferromagnetic coupling with antisite Mn atoms.

**ACKNOWLEDGMENTS**

This research was supported by DOE (DE-F602-04ER46152) (DJS, RS), NSF MRSEC (NSF-DMR-0820521) (PK, YH), NSF MRI TEM (DMR-0960110) and NCMN (VRS, XZL). We would like to thank J. E. Shield for using his sample preparation facility.

18. TOPAS-V 4.2, Bruker AXS, Inc.