Ferrimagnetism in sputtered Mn$_x$CoGe thin films

D. Kalliecharan,$^1$ J. S. R. McCoombs,$^1$ M. M. E. Cornier,$^1$ B. D. MacNeil,$^1$ R. L. C. Molino,$^1$ and T. L. Monchesky$^{1,*}$

$^1$Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5
(Dated: October 2, 2019)

Investigations into the magnetic properties of sputtered Mn$_x$CoGe films in the range $0.8 \leq x \leq 2.5$ uncovered ferrimagnetic order, unlike the ferromagnetic order reported in bulk samples. These films formed hexagonal Ni$_2$In-type structures in all measured compositions. While the Curie temperatures of the films are comparable to those of hexagonal bulk MnCoGe, there is a reduction in the magnetization of the Mn$_x$CoGe film relative to bulk MnCoGe, and a magnetization compensation point is observed in the $x < 1$ samples. To understand the behavior, we calculated the magnetic moments of Mn-antisite defects in MnCoGe with density-function theory calculations. Models constructed from the calculation suggest that films become ferrimagnetic due to the presence of Mn on the Co and Ge sites. In the $x < 1$ samples, these defects arose from the disorder in the films, whereas for $x > 1$, the excess Mn was driven onto the antisites and produced ferrimagnetic order.

I. INTRODUCTION

The manganese germanides provide a rich phase diagram with a diverse range of magnetic structures. Mn$_3$Ge forms one of two polytypes. The Mn$_3$Ge D0$_{19}$ hexagonal structure is a frustrated non-collinear antiferromagnet with a large topological Hall effect$^{1}$, while the tetragonal D0$_{22}$ Heusler is a high-anisotropy ferrimagnet of interest for memory applications$^{2}$. There have been recent proposals for tuning the magnetic properties of this structure via chemical substitutions Mn$_{3-x}$X$_x$Ge$^2$. Substitution of Ni, for example, decreases the moment and increases the coercivity.$^4$

A related family of compounds – the inverse tetragonal Heuslers – is obtained by replacing Mn on one of the 4d Wyckoff sites in the D0$_{22}$ structure, (0, 1/2, 1/4), with another element. This lowers the symmetry from $D_{4h}$ to the non-centrosymmetric $D_{2d}$ point group and turns on the Dzyaloshinskii-Moriya interaction that is responsible for the non-collinear magnetic structures in Mn$_2$RhSn$^5$ and Mn$_{1.4}$PtSn$^5$. The stability of the Mn$_2$XGe Heusler compounds have been explored by density-functional theory (DFT) calculations$^2$, many of which are predicted to form the inverse tetragonal structure, including Mn$_2$CoGe. The initial motivation for the work in this paper was to create Mn$_2$CoGe Heusler alloy films by magnetron sputtering. We fabricated Mn$_x$CoGe in the compositional range $0.8 \leq x \leq 2.5$, but were unsuccessful in producing Heusler alloys. The entire composition formed either a hexagonal structure or an orthorhombic structure related to the magnetocaloric material, MnCoGe.

At low temperature, MnCoGe forms an orthorhombic C23 TiNiSi-type structure (space group #62, Pnma). It is a collinear ferromagnet with a Curie temperature, $T_C^{\text{ortho}} = 355$ K and a magnetic moment of $m = 3.86\mu_B$/formula unit (f.u.). At a temperature $T_t$, the material undergoes a martensitic transformation to a hexagonal B8$_2$ Ni$_2$In-type structure (space group #194 P6$_3$/mmc). The resulting 3.9% contraction in volume leads to a broadening of the Mn d-bands producing a smaller moment and lower $T_C^{\text{hex}}$. In this hexagonal polytype, $m = 2.78\mu_B$/f.u.$^{15}$ and $T_C^{\text{hex}} \approx 260$ K. The martensitic transition is very sensitive to defects. Johnson et al. found that $T_t$ varied between 398 – 453 K, while Kanomata et al. reported $T_t$ as high as 650 K. When $T_t$ lies between $T_C^{\text{hex}}$ and $T_C^{\text{ortho}}$ the material undergoes a first-order transition from an orthogonal ferromagnet, to a hexagonal paramagnet that gives rise to a large magnetocaloric effect.

![FIG. 1. The primitive unit cell of MnCoGe Ni$_2$In-type phase. Isometric view (top) and c-axis projection (bottom), showing the 2a-Mn sites (gray), the 2c-Co sites (red) and 2d-Ge sites (blue).](image_url)

What makes MnCoGe particularly attractive is that its martensitic temperature can be chemically tuned independent of $T_C$. The transition temperature $T_t$ is very sensitive to Co vacancies$^{11,12}$ as well as Mn vacancies$^{13}$. With only a few percent vacancies on either site, $T_t$ can be reduced to room temperature with little effect on either $T_C^{\text{hex}}$ or $T_C^{\text{ortho}}$. This is potentially driven by a reduction in the number of valence electrons, as the same effect is also observed in Mn$_{1+x}$Co$_{1−x}$Ge alloys.$^{13,14}$ Numerous studies have explored the influence of other defects and...
substitutions in MnCoGe; a comprehensive summary of such studies is given in the appendix of Ref. 15.

In the Ni$_2$In-phase, Mn resides on the 2a (0,0,0) Wyckoff sites and forms low density (001) planes. These are separated by dense CoGe planes with Co on the 2c (1/3, 2/3, 1/4) sites and Ge on the 2d (2/3, 1/3, 1/4) sites (see Fig. 1). We found that Mn$_x$CoGe films prepared by DC magnetron sputtering were much more disordered than typical bulk material, which had two important consequences. Firstly, the hexagonal B8$_2$ phase was obtained at room temperature after annealing at $T = 500 \, ^\circ\text{C}$ and remained in this phase upon cycling down to low temperature, consistent with other reports of sputtered MnCoGe films. Secondly, the films display ferrimagnetic rather than ferromagnetic order reported in other investigations of this material. We support the analysis of the magnetic properties with DFT calculations that show the spins from Mn-antisite defects align in the opposite direction to the spins on the Mn-sites.

II. GROWTH

Films were deposited on thermally oxidized wafers, as SiO$_2$ acts as a diffusion barrier for Mn, Co and Ge. Si(001) wafers (manufactured by Prolog semiconductor Ltd.) were cut into 20 mm × 20 mm squares and were sonicated in acetone and methanol baths for 15 minutes each. Before removing the wafers from the methanol bath, deionized nanopure water was slowly added and allowed to overflow in order to remove any contaminants from the liquid surface. The wafers were heated in a dry furnace at 900 °C for 5 hours to create a SiO$_2$ layer, approximately 300 nm in thickness.

The sonication treatment was then repeated prior to loading samples into a Corona Vacuum Coater V3T magnetron sputtering deposition system with a base pressure of 3.0 × 10$^{-7}$ Torr. The Ar pressure during sputtering was 2.0 × 10$^{-3}$ Torr. Sputtering rates were calibrated by measuring the weights of the samples before and after growth. The compositions were verified using a Thermo iCAP Q laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS). The results are shown in Table I.

The as-grown amorphous films where crystallized ex-situ by annealing in an Ar environment in a Modular Process Technology RTP600s Rapid Thermal Anneler (RTA). The RTA reached the desired temperatures within 20 s (15–35 °C/s), and were cooled at a rate of approximately 2 °C/s.

III. STRUCTURAL CHARACTERIZATION

The crystal structures of the films were investigated with conventional X-ray diffraction (XRD) $\theta$ – 2$\theta$ measurements on a Siemens D500 Diffractometer equipped with a Cu source and monochromator. To determine the strain in the films, the XRD measurements were compared to grazing angle X-ray diffraction (GAXRD) measurements, where the incident X-ray beam is fixed at $\theta_i = 6^\circ$. The alignment of the diffractometer was checked with a Si powder sample for both the XRD and the GAXRD geometries.

Annealing times and temperatures were selected to produce single phase samples. Five sets of samples – Mn$_{0.8}$CoGe, Mn$_{0.9}$Co$_{0.8}$Ge, Mn$_{1.4}$CoGe, Mn$_{1.8}$Co$_{0.6}$Ge and Mn$_{2.5}$CoGe – were annealed within the temperature range of 375 °C - 500 °C for an interval time between 2 minutes and 40 minutes, yielding Ni$_2$In-type polycrystalline films. High temperature annealing resulted in mixed phase samples: annealing at 700 °C produced a mixture of Ni$_2$In-type and TiNiSi-type phases, but there was no evidence of a tetragonal phase. Figure 2 shows fits to GAXRD measurements of the Ni$_2$In-type samples that demonstrate the phase is stable across the entire composition range, 0.8 ≤ x ≤ 2.5.

The lattice parameters extracted from the GAXRD fits (Table I), are comparable to the values of bulk MnCoGe, $a = 4.087(1)$, $c = 5.316(3)$ Å. The Rietveld refinements were performed using Rietica version 4.0 (http://rietica.org). We note that the (101) peak intensity is much lower than expected from bulk MnCoGe samples. The discrepancy could be accounted for with 20% vacancies on the 2c-site occupied by Co. The presence of vacancies is consistent with ICP-MS measurements that show Mn concentrations are lower than the nominal value. The intensity of the (210)-peaks is higher than expected. As the annealing process can lead to preferred grain orientation, it is not possible to separate this effect from the possibility of vacancies.

| $x$ | $\chi_{\text{Mn}}/\chi_{\text{Ge}}$ | $\chi_{\text{Co}}/\chi_{\text{Ge}}$ | c (Å) | a (Å) |
|-----|-------------------------------|-------------------------------|-------|-------|
| 0.8 | 0.79                          | 0.93                          | 4.02  | 5.21  |
| 0.9 | 0.89                          | 0.79                          | 4.03  | 5.23  |
| 1.4 | 1.42                          | 0.97                          | 4.05  | 5.30  |
| 1.8 | 1.83                          | 0.78                          | 4.05  | 5.36  |
| 2.5 | 2.47                          | 1.07                          | 4.07  | 5.29  |

The GAXRD peak positions were found to be systematically lower than the XRD measurements (unlike the control Si powder sample). A comparison between GAXRD and XRD is shown in Fig. 3a). While XRD probes the lattice parameters of planes that are parallel to the substrate surface, GAXRD measures interatomic planes whose normal is further and further from the film normal as the detector angle $\theta$ increases. We define $\phi = \theta - \theta_i$ as the angle between this normal and the film’s normal. As shown below, the shift in the GAXRD peaks relative to those in the conventional XRD measurements is due to strain in the films. To determine the influence of film strain on the GAXRD measurements, we assume
a uniform biaxial strain of the polycrystalline material, where $\epsilon_\perp$ and $\epsilon_\parallel$ are the out-of-plane and in-plane strains in the film, respectively. We obtain an expression for the atomic plane spacing, $d(\phi)$ for planes that are at an angle $\phi$ with respect to the film surface,

$$
d(\phi) = d(0) \left( 1 + 2\epsilon_\parallel \sin^2 \phi + 2\epsilon_\perp \cos^2 \phi \right)^{\frac{1}{2}},
$$

in terms of the plane spacing measured by XRD, $d(0)$. For small strain and small $\phi$, $d(\phi) \approx d(0)(\epsilon_\parallel - \epsilon_\perp)\phi^2$. Figure 3b shows a fit to $d(\phi)$ for the Mn$_{1.4}$CoGe sample, which gives $\epsilon_\parallel - \epsilon_\perp = 0.07 \pm 0.01$.

The strain, which was observed for all Mn$_x$CoGe films, is likely induced by the annealing process. The thermal expansion coefficients for metals is typically about one order of magnitude larger than the Si substrate. The film crystallizes at high temperature; since the film contracts more than the substrate upon cooling, the film develops an in-plane tensile strain (and through the Poisson ratio, it develops an out-of-plane compressive strain).

FIG. 2. XRD data (black) with Reitveld refinements (orange), residuals (blue) and Ni$_2$In-type peak locations (green): (a) Mn$_{0.8}$CoGe, (b) Mn$_{0.9}$Co$_{0.8}$Ge, (c) Mn$_{1.4}$CoGe, (d) Mn$_{1.8}$Co$_{0.8}$Ge and (e) Mn$_{2.5}$CoGe, with hexagonal (green) peak locations in (f).

FIG. 3. (a) XRD and GAXRD measurements of Mn$_{1.4}$CoGe. The lower panel shows the XRD peak positions relative to GAXRD peaks. Note that in order to be able to see the (202) peak in the XRD data, the intensity of the Si(004) peak at $2\theta = 69.9$ was reduced by offsetting the sample angle by 2$^\circ$. (b) The normalized change in the interatomic plane spacing as a function of the angle the planes make with the film surface. The solid line show the fit to the data using Eq. (1).
IV. MAGNETIC MEASUREMENTS

Magnetic measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS), equipped with a P500 AD/DC Magnetometry System (ACMS). Samples were cut into 5.8 mm × 5.8 mm squares and wedged into a plastic straw that was placed in the PPMS. The field was applied in the plane of the film.

Magnetization loops were recorded as the field was cycled between $\mu_0 H = +9$ T and -9 T. The $M - H$ loops for all 5 samples measured at $T = 5$ K are qualitatively similar, as shown in Fig. 4(b). However, hysteresis loops with $x > 1$ show higher $H_C$ and more rounding, suggestive of a larger mean effective anisotropy with a broader distribution.

The remanent magnetization, $M_R$, was measured on warming from $T = 5$ K after saturating the film in a 9 T field. The temperature dependence of $M_R$ is shown in Fig. 5. The shape of the $M_R - T$ graph for the $x = 2.5$ sample (shown in yellow) is typical of a ferromagnet. Some of the $x = 2.5$ samples had a small remanent magnetization above $T = 270$ K. Although no impurity phase could be detected in the X-ray measurements, additional annealing in the RTA was able to remove this additional ferromagnetic contribution. The $x = 1.4$ and 1.8 samples also show a small $M_R$ above $T = 270$ K but further annealing could not remove the impurity phase. Unexpectedly, the compositions with $x < 1$ showed ferrimagnetic behavior: above a compensation point of approximately 230 K, the $M_R$ reverses sign.

The Curie temperature is estimated from the temperature where $M_R$ goes to zero. As shown in the Table II, $T_C$ is comparable to the bulk $T_C$ of the hexagonal phase, and is relatively insensitive to the composition $x$, as observed in bulk[11]. However, the table also shows that the total magnetic moment per primitive unit cell is significantly lower than the bulk value for MnCoGe, 5.56$\mu_B$ per primitive unit cell.

| $x$ | $M_S$ (kA/m) | $m$ ($\mu_B$) | $H_C$ (mT) | $T_C$ (K) |
|-----|--------------|---------------|------------|-----------|
| 0.8 | 380          | 2.99          | 26         | 267       |
| 0.9 | 384          | 3.02          | 20         | 260       |
| 1.4 | 497          | 4.19          | 78         | 277       |
| 1.8 | 394          | 3.19          | 69         | 272       |
| 2.5 | 353          | 2.87          | 89         | 267       |

TABLE II. The saturation magnetization, $M_S$, the magnetic moment per primitive unit cell, $m$, the coercive field $\mu_0 H_{ext}$ and Curie Temperature $T_C$ for Mn$_x$CoGe films.

V. COMPUTED MAGNETIC MOMENTS FROM DENSITY-FUNCTIONAL THEORY

To explore the origin of the drop in magnetic moment and the appearance of ferrimagnetic behavior, we considered the influence of atomic disorder in the Ni$_2$In structure on the individual magnetic moments. In the ordered phase, nuclear magnetic resonance (NMR) shows that Mn on the 2a-site has a magnetic moment of $m_{Mn} = 2.4$ $\mu_B$, while the moment of Co on the 2c-site couples ferromagnetically to the 2a-site with a moment $m_{Co} = 0.4$ $\mu_B$. These values are in good agreement with the measured magnetization and consistent with neutron scattering experiments[10]. However, we note that DFT overestimates the magnetic moment of Mn in MnCoGe[2,10,20], and so has to be rescaled to compare to experiment.

Previously published DFT calculations of Ni$_2$In-type Mn$_2$Ge predict ferrimagnetic behavior due to the antiparallel coupling between Mn on 2a- and 2c-sites[21]. This is consistent with tight-binding (TB) calculations for
MnCoGe that show a reduction in the average Mn moment when it is distributed on both of these sites. The TB calculations show that Co on the other hand is little affected by either moving it to the 2a-site, or by the presence of Mn-antisite defects, as supported by DFT calculations. However, there are very few studies of the Ni$_2$In-type structure and it remains unclear exactly what is the magnetic behavior of Mn on the 2c- and 2d-sites (Mn$_{2a}$ and Mn$_{2d}$).

DFT computations were performed within the spin-polarized general gradient approximation (GGA) using the Vienna Ab-initio Simulation Package (VASP). Local magnetizations are obtained by projecting the ground state crystal orbitals onto atomic-like orbitals centered at each crystallographic site (i.e. atom-centered). Since the magnetization can be strongly dependent on the inter-atomic distances, full cell relaxations were performed for all structures, converging forces to better than 0.01 eV/Å and stresses to within 0.001 GPa by enforcing a sufficiently dense k-point sampling of the first Brillouin zone. We used projector augmented wave (PAW) datasets with 7, 9, and 4 valence electrons for Mn, Co, and Ge, respectively. The ground state energies were converged to better than 1 meV/f.u. using a plane-wave energy cut-off of 550 eV. We attempted to converge both ferromagnetic and ferrimagnetic solutions for all structures. In some cases both solutions converged, but we present here only the lowest energy solutions.

Our computed magnetic moments for Ni$_2$In-type MnCoGe and Mn$_2$Ge agree well with previously calculated values. In MnCoGe, our computations show a slightly smaller Mn moment, $2.75 \mu_B$ compared to the value calculated in Ref. 20 (3.09 $\mu_B$), but one that is closer to the experimental value. We obtain a moment of 0.5$\mu_B$ on Co, and $-0.1\mu_B$ on Ge that are in good agreement with Ref. 20, as well as experimental values. In Mn$_2$Ge, our computed magnetizations for Mn$_{2a}$, 2.9 $\mu_B$ and Mn$_{2c}$, -2.0 $\mu_B$, agree exactly with previously published DFT results.

To determine the effect of Mn$_{2c}$, $2 \times 2 \times 2$ supercells were built by repeating the MnCoGe hexagonal unit cell (6 atoms) twice along each lattice vector resulting in 16 Mn, 16 Co, and 16 Ge atoms. We considered the Mn$_{1+y}$Co$_{1-y}$Ge solid solution where the excess Mn, y, replaces Co on the 2c site. For the dilute limit we placed 1 Mn on the 2c-site per supercell ($y = 0.06$); in the concentrated limit 15 of the 16 2c-sites were occupied by Mn ($y = 0.94$). We note that the case of $y = 0$ and $y = 1$ correspond to MnCoGe and Mn$_2$Ge. The results are shown in Fig. 6.

The Mn$_{2c}$ has little impact on the magnetic moments of either the Mn$_{2a}$ moments or the Co or Ge moments. However Mn$_{2c}$ does have a significant compositional dependence and is antiferromagnetically coupled to the Mn$_{2a}$ moments. In the dilute limit, the Mn$_{2c}$ moment $-0.6 \mu_B$ is opposite in sign but comparable in magnitude to the Co moment. The magnetic moment of Mn$_{2c}$ reached $-1.86 \mu_B$ in the concentrated Mn$_{2c}$ regime, which approaches the calculated value for Mn$_2$Ge, as expected.

We additionally performed DFT calculations for Mn...
substituted on the 2d-site (Mn$_{2d}$). From the $2 \times 2 \times 2$ supercells, 1 of the 15 Ge atoms was replaced by Mn to give Mn$_{1.06}$CoGe$_{0.94}$. To examine the influence of Mn on both the 2c- and 2d-sites, we replaced 1 Co and 1 Ge atom in the supercell with Mn to give Mn$_{1.12}$Co$_{0.93}$Ge$_{0.88}$. Two different configurations of this stoichiometry were generated – one where the Mn on the 2c-site was nearest to the Mn on the 2d-site, another where it was farthest. All three configurations resulted in the same magnetic moment of $-2.9 \mu_B$ for Mn on the 2d-site and an unchanged magnetic moment for Mn on both the 2a- and 2c-sites.

VI. DISCUSSION

To interpret the magnetometry measurements, we construct a simple model from the DFT determined magnetic moments. We first assume that the Mn on the 2d-site, another where it was farthest. All three configurations resulted in the same magnetic moment of $-2.9 \mu_B$ for Mn on the 2d-site and an unchanged magnetic moment for Mn on both the 2a- and 2c-sites.

\begin{equation}
2a : \text{Mn}_{x+2}/3 - \delta \text{Co}_\delta,
2c : \text{Mn}_{x-1}/3 + \delta \text{Co}_{1-\delta},
2d : \text{Mn}_{x-1}/3 \text{Ge}.
\end{equation}

In the case of Mn deficient Mn$_x$CoGe samples, $x < 1$, the excess Co and Ge are also assumed to be evenly distributed on the 2a-sites. When site disorder is added into the model, the elemental distribution becomes,

\begin{equation}
2a : \text{Mn}_{x-\delta} \text{Co}_{(1-x)/3 + \delta} \text{Ge}_{(1-x)/3},
2c : \text{Mn}_{\delta} \text{Co}_{(2+x)/3 - \delta},
2d : \text{Ge}_{(2+x)/3}.
\end{equation}

In our model, we use the experimentally determined moments, $m_{\text{Mn}_{2a}} = 2.4 \mu_B$ and $m_{\text{Co}_0} = 0.4 \mu_B$. We are not aware of any measurement of the Mn moment on the 2c-site, particularly not as a function of excess Mn. We therefore use a linear approximation to estimate compositional dependence of the Mn$_{2c}$ magnetic moment computed from our DFT calculations. From the DFT results in Fig. 6, we expect that the Mn moment on the 2c-sites in Mn$_x$CoGe would be approximately give by,

\begin{equation}
m_{\text{Mn}_{2c}}(x) = -1.43 \left( \frac{x - 1}{x + 2} \right) - 0.514,
\end{equation}

in units of $\mu_B$. Since DFT overestimates the Mn moment on the 2a-site by a factor (2.4/2.75), we rescale the above DFT prediction by the same amount. Finally, we use a constant $m_{\text{Mn}_{2d}} = -2.9$ for the Mn antisite defects on the 2d-sites, as determined from our DFT calculations.

A further refinement of the model includes 20% Co vacancies (on the 2c site), which is the maximum amount of vacancies extracted from XRD fits assuming no preferred orientation, although this was found to have a relatively small effect on the total moment per unit cell. The calculated magnetic moment as a function of $x$ and $\delta$ is shown by the lines and colour plot in Fig. 7. The white lines show the magnetic moment per unit cell for two different levels of disorder. Below $x = 1$, the modelled moment drops with decreasing $x$ due to a reduction in the available Mn. Above $x = 1$, the moment drops with increasing $x$ as more Mn is forced onto the 2c-sites and 2d-sites. The colour scale reflects the decrease in magnetic moment with Co$_{2a}$: a comparison with the data points allows an estimation of the disorder, $\delta$. The disorder is as large as $\delta = 0.3$ at $x = 0.9$ and drops to $\delta = 0.07$ at $x = 2.5$. Despite informing our model with the detailed results of our DFT calculations, disorder is required to explain the ferrimagnetic behavior observed in Fig. 4 and the lower than expected magnetic moment. The absence of a compensation point in the higher Mn-content samples suggest that the alloy transitions from a Q-type ferrimagnetic (e.g. Y$_3$Ga$_{0.5}$Fe$_{4.5}$O$_{12}$) to an N-type (e.g. Y$_3$Ga$_{3}$Fe$_{7.5}$O$_{12}$) at larger $x$. Neutron scattering experiments are required to test this hypothesis.

VII. CONCLUSION

Sputtered Mn$_x$CoGe compounds formed a hexagonal Ni$_2$In-type structure over the entire compositional range...
0.8 ≤ x ≤ 2.5 explored in this study. The unexpected ferrimagnetic behavior is explained by the incorporation of a fraction of the Mn onto either the 2c- or 2d-sites where DFT calculations show it couples antiferromagnetically to the 2a-sites. The possibility of changing a film from ferromagnetic to ferrimagnetic through the growth process is potentially interesting for other material systems in the context of spintronics, as the reduced moment of the ferrimagnet potentially makes it more efficient to switch with spin-transfer torque or spin-orbit torque.

VIII. ACKNOWLEDGMENTS

We would like to thank Prof. Jeff Dahn for use of the sputtering machine. We would also like to thank Andrew George and Michel Johnson for technical assistance with XRD and PPMS measurements, and finally, James Brennan and Erin Keltie for assistance in training and analysis with LA-ICP-MS measurements.

* tmonches@dal.ca

1 Ajaya K. Nayak, Julia Erika Fischer, Yan Sun, Binghai Yan, Julie Karel, Alexander C. Komarek, Chandra Shekhar, Nitesh Kumar, Walter Schnelle, Jürgen Kübler, Claudia Felser, and Stuart S. P. Parkin. Large anomalous hall effect driven by a nonvanishing berry curvature in the noncolinear antiferromagnet Mn$_2$Ge. Sci. Adv., 2(4), 2016.

2 H. Kurt, N. Baadj, K. Rode, M. Venkatesan, P. Stanenov, S. Sanvito, and J. M. D. Coey. Magnetic and electronic properties of d022-Mn$_2$Ge (001) films. Appl. Phys. Lett., 101(13):132410, Sep 2012.

3 Yurong You, Guizhou Xiu, Fang Hu, Yuanyuan Gong, Er Liu, Guo Peng, and Feng Xu. Designing magnetic compensated states in tetragonal Mn$_2$Ge-based heusler alloys. J. Magn. Magn. Mater., 429:40–44, 2017.

4 Jan Balluff, Jan-Michael Schmalhorst, Elke Arenholz, Markus Meineit, and Ginter Reiss. Enhancing magnetic properties in Mn$_2$Ge thin films by doping. Phys. Rev. B, 97:014403, Jan 2018.

5 O. Meshcheriakova, S. Chadov, A. K. Nayak, U. K. Rössler, J. Kübler, G. André, A. A. Tsirlin, J. Kiss, S. Hausdorf, A. Kalache, W. Schnelle, M. Nicklas, and C. Felser. Large nonlinearity and spin reorientation in the novel Mn$_2$RhSn heusler magnet. Phys. Rev. Lett., 113:087203, Aug 2014.

6 Ajaya K. Nayak, Vivek Kumar, Tianping Ma, Peter Werner, Eckhard Pippel, Roshnee Sahoo, Françoise Damay, Ultrach K. Rößler, Claudia Felser, and Stuart S. P. Parkin. Magnetic antiskyrmioms above room temperature in tetragonal heusler materials. Nature, advance online publication 548:561–566, 08 2017.

7 Sergey V. Faleev, Yari Ferrante, Jaewoo Jeong, Mahesh G. Samant, Barbara Jones, and Stuart S. P. Parkin. Origin of the tetragonal ground state of heusler compounds. Phys. Rev. Applied, 7:034022, Mar 2017.

8 V. Johnson. Diffusionless orthorhombic to hexagonal transitions in ternary silicides and germanides. Inorg. Chem., 14(5):1117–1120, 05 1975.

9 S. Kaprzyk and S. Niziol. The electronic structure of congane with the hexagonal and orthorhombic crystal structure. J. Magn. Magn. Mater., 87(3):267–275, 1990.

10 T. Kanomata, H. Ishigaki, K. Sato, M. Sato, T. Shinhara, F. Wagatsuma, and T. Kaneko. NMR study of $^{53}$Mn and $^{59}$Co in MnCoGe. J. Magn. Soc. Jpn., 23(1-2):418–420, 1999.

11 T. Kanomata, H. Ishigaki, T. Suzuki, H. Yoshida, S. Abe, and T. Kaneko. Magneto-volume effect of MnCo$_{1-x}$Ge (0 ≤ x ≤ 0.2). J. Magn. Magn. Mater., 140-144:131–132, 1995.

12 Yi-Kun Fang, Jia-Chun Yeh, Wen-Cheng Chang, Xiu-Mei Li, and Wei Li. Structures, magnetic properties, and magnetocaloric effect in MnCo$_{1-x}$Ge (0.02<x<0.2) compounds. J. Magn. Magn. Mater., 321(19):3053–3056, 2009.

13 E. K. Liu, W. Zhu, L. Feng, J. L. Chen, W. H. Wang, G. H. Wu, H. Y. Liu, F. B. Meng, H. Z. Luo, and Y. X. Li. Vacancy-tuned paramagnetic/ferromagnetic martensitic transformation in Mn-poor Mn$_{1-x}$Co$_x$Ge alloys. EPL, 91(1):17003, 2010.

14 Sheng-Can Ma, Dun-Hui Wang, Hai-Cheng Xuan, Ling-Jia Shen, Qing-Qi Cao, and You-Wei Du. Effects of the Mn/Co ratio on the magnetic transition and magnetocaloric properties of Mn$_{1+x}$Co$_{1-x}$Ge alloys. Chinese Physics B, 20(8):087502, 2011.

15 Qingyong Ren. New materials for magnetic refrigeration: the magnetocaloric effect in MnCoGe-based intermetallics. PhD thesis, The University of New South Wales, School of Physical, Environmental, and Mathematical Sciences, April 2016.

16 A. Portavoce, E. Assaf, C. Alvarez, M. Bertoglio, R. Clérac, K. Hounmada, C. Alfonso, A. Charaï, O. Pilon, K. Hahn, V. Dolocan, and S. Bertaina. Ferromagnetic mucoge thin films produced via magnetron sputtering and non-diffusive reaction. Appl. Surf. Sci., 437:336–346, 2018.

17 Yota Takamura, Ryosho Nakane, Hiro Munekata, and Satoshi Sugahara. Characterization of half-metallic L1$_2$-phase Co$_2$FeSi full-Heusler alloy thin films formed by rapid thermal annealing. J. Appl. Phys., 103(7):1–4, 2008.

18 W. Jeitschko. A high-temperature X-ray study of the discommensuration order in Mn$_2$Ge. Acta Crystallogr. B, 31(4):1187–1190, Apr 1975.

19 S. Kaprzyk and S. Niziol. The electronic structure of CoMnGe with the hexagonal and orthorhombic crystal structure. J. Magn. Magn. Mater., 87(3):267–275, jul 1990.

20 Konstanze R. Hahn, Elie Assaf, Alain Portavoce, Sylvain Bertaina, and Ahmed Charaï. Structural and Composition Effects on Electronic and Magnetic Properties in Thermoelectric Mn$_{1-x}$Co$_{1+y}$Ge$_{1+y}$ Materials. The Journal of Physical Chemistry C, 121(48):26575–26586, dec 2017.

21 M. Ellner. Kristallstrukturdaten von Mn$_2$Ge. J. Appl. Crystallogr., 13(1):99–100, 1980.

22 Konstanze R. Hahn, Elie Assaf, Alain Portavoce, Sylvain Bertaina, and Ahmed Charaï. Structural and composition effects on electronic and magnetic properties in thermoelectric Mn$_{1-x}$Co$_{1+y}$Ge$_{1+y}$ materials. The Journal of Physical Chemistry C, 121(48):26575–26586, 12 2017.
P. Hohenberg and W. Kohn. Inhomogeneous Electron Gas. 
*Phys. Rev.*, 136(3B):B864–B871, 1964.

Walter Kohn and L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. Lett.*, 140(4A):1133–1138, 1965.

John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 77(18):3865–3868, 1996.

G. Kresse and J. Hafner. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B*, 47(1):558–561, 1993.

G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54(16):11169–11186, 1996.

G Kresse and D Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59(3):11–19, 1999.

G Kresse and J Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.*, 99(1):16–29, 2007.

Emmanuel Arras, Damien Caliste, Thierry Deutsch, Frédéric Lançon, and Pascal Pochet. Phase diagram, structure, and magnetic properties of the ge-mn system: A first-principles study. *Phys. Rev. B*, 83:174103, May 2011.

S. Chikazumi and C.D. Graham. *Physics of Ferromagnetism 2e*. International Series of Monogr. OUP Oxford, 2009.