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A Nanolaminated Magnetic Phase: Mn_2GaC

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Supplementary Material Available Online

We report on first principles prediction and subsequent synthesis of Mn_2GaC , a new member of the inherently nanolaminated $M_{n+1}AX_n$ (MAX) phase family. This phase, the first to include Mn as the sole M element, was synthesized as a heteroepitaxial thin film. The material was theoretically predicted to display magnetic ordering with ferromagnetic (FM) and antiferromagnetic configurations degenerate in energy within the computational accuracy. Vibrating sample magnetometer measurements show FM ordering with a saturation moment of $m_s = 0.29 \mu\text{B}$ per Mn atom and remanent moment of $m_r = 0.15 \mu\text{B}$ per Mn atom for temperatures $\leq 230 \text{ K}$.

Keywords: MAX Phases; Magnetism; Thin Films; First Principles Calculations; Phase Stability

Since their discovery in the 1960s [1,2] and a later revival by Barsoum,[3] the $M_{n+1}AX_n$ (MAX) phases ($n = 1 - 3$) have received an ever increasing level of attention. They are a family of around 60 phases composed of a transition metal (M) an A-group element (A) and carbon or nitrogen (X), with the different elements forming individual atomic layers.[4] Early work on these materials has been focused on their unique mechanical properties, including strength, ductility, thermal conductivity, resistance to oxidation, etc.[3] Later studies have explored, e.g. reversible deformation [5] and stability of nanosheets upon exfoliation.[6] With recent improvements in heteroepitaxial growth, attention has shifted towards measurements of their more subtle properties which require high crystal quality.

Interest in magnetism in MAX phases is substantial since magnetism combined with the nanolaminated structure and suggested tunable anisotropic transport properties [7] could potentially allow the fabrication of functional MAX phases for various applications in spintronics. Metals that are known M elements in MAX phases [4] are the early transition metals Sc, Ti, V, Cr, Zr, Nb, Mo, Hf and Ta, but none of these form MAX

phases with ferromagnetic (FM) behavior. In order to realize the full potential of these nanolaminates in spintronics, there is therefore a need to expand the family of M elements.

Dahlqvist et al. have developed an *ab initio* approach [8] to theoretically determine the stability of MAX phases and have successfully applied this approach to confirm the stability of a large set of existing phases [9] as well as predicting the existence of the previously unknown Nb_2GeC [10] phase. Furthermore, a systematic theoretical study of alloying Cr_2AC ($A = \text{Al}, \text{Ge}$) with Mn showed that by substituting Cr with Mn, the resulting phases were endowed with magnetic properties with various magnetic ordering depending on the Cr/Mn ratio and internal ordering.[11,12]

Here, we report on the theoretical prediction of a stable but unexplored MAX phase: Mn_2GaC . We present subsequent thin film synthesis of this phase and experimental confirmation of theoretically predicted magnetic properties. Mn has recently been investigated as an alloying element with other known M elements in MAX phases.[12–14] However, the present study is the first to exclusively include a previously

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unknown M element, since the initial discovery of MAX phases.[2]

For evaluation of phase stability, *ab initio* calculations based on density functional theory were performed using the projector augmented wave method [15] as implemented within the Vienna *ab-initio* simulation package (VASP).[16,17] Exchange and correlation effects were treated in the framework of the Perdew–Burke–Ernzerhof [18] generalized gradient approximation in its spin-polarized form. We have used a plane wave energy cutoff of 400 eV, and integration of the Brillouin zone was performed using the Monkhorst–Pack scheme.[19] The calculated total energy for all phases included in the present study are converged to within 0.1 meV/atom in terms of k-point sampling and plane wave energy cutoff. Structural optimizations were performed for each phase in terms of unit-cell volumes, cell shape and internal atomic positions to minimize the total energy. Nonmagnetic, paramagnetic, FM and different antiferromagnetic (AFM) states were tested for each phase and the configuration with the lowest energy was included in the phase stability investigation (see Supplemental Material). In order to predict the stability of a $\text{Mn}_{n+1}\text{GaC}_n$ phase, we identify a set of most competing phases (cp) at the $\text{Mn}_{n+1}\text{GaC}_n$ ($n = 1 - 3$) composition, with corresponding stability expressed in terms of formation enthalpy given by $\Delta H_{\text{cp}} = H[\text{Mn}_{n+1}\text{GaC}_n] - H_{\text{total}}[\text{cp}]$. ΔH_{cp} is obtained through a linear optimization procedure based on the simplex method, where all experimentally known competing phases within the Mn–Ga–C system, as well as hypothetical competing phases based on neighboring and similar systems, are included.[8,9] Even though the method only accounts for the enthalpy, excluding effects from entropy, it has been shown to reproduce completely the stability of existing MAX phases for a rather large set of well-known carbide and nitride systems, see e.g. [9].

ΔH_{cp} for $\text{Mn}_{n+1}\text{GaC}_n$ is presented in Table 1. Only Mn_2GaC ($n = 1$) is stable with $\Delta H_{\text{cp}} = -30$ meV/atom. This can be compared with calculated ΔH_{cp} of synthesized MAX phases, e.g. Nb_2GeC (-18 meV/atom),[10] Ti_2AlC (-37 meV/atom),[9] and Cr_2GeC (-62 meV/atom).[20]

For Mn_2GaC , we find the magnetic ground state to be practically degenerate between FM and AFM[0001] $_2^4$, the latter notation referring to the predicted double layer AFM equivalent to those described in [21]. Both magnetic

states are dynamically stable, i.e. stable relative to lattice vibrations, evident from the lack of imaginary phonon frequencies in the phonon spectrum (see Supplemental Material).

Thin films were deposited by magnetron sputter epitaxy (MSE) using three confocal sources with elemental targets: carbon (99.99% purity), manganese (99.95% purity) and gallium (99.99995% purity). Due to the low melting temperature of Ga (29°C), the target was kept in a specially designed stainless steel crucible positioned directly under the substrate. An appropriate amount of Ga ingots were melted into the crucible and the material was then cooled down and solidified before introduction into the deposition system. The Ga target melts due to heating from the plasma and was kept liquid throughout the deposition for consistency. The base pressure in the ultra high vacuum (UHV) system was $\leq 5 \times 10^{-9}$ Torr before deposition, and at an Ar pressure of 4.5 mTorr during depositions. The MgO (111) substrates were cleaned in ultrasonic baths of acetone, ethanol and isopropanol for 10 min and then kept at the deposition temperature of 550°C for 60 min prior to deposition to ensure uniform heat distribution. The current applied to the targets was regulated and the sputtering rates of Mn and C were calibrated to give a 2:1 ratio. Due to the low melting temperature of Ga and the different dynamics of a liquid target,[20] the applied current was fine tuned in order to optimize the growth rate. Further information regarding the co-sputtering including a Ga target can be found in [20].

Structural information was obtained by X-ray diffraction (XRD) and reflection using a Panalytical Empyrean MRD system equipped with a Cu $K\alpha$ source. For $\theta - 2\theta$ measurements the tube was in line focus with a hybrid mirror on the incident side and a 0.27° collimator on the diffracted side. Pole figure measurements were performed with the tube in point focus, using a capillary X-ray lens on the incident side with a spot opening of 1×1 mm and a 0.27 collimator on the diffracted side. Figure 1 shows a $\theta - 2\theta$ scan of the film. The only substantial peaks seen in the figure are the film basal 0001 peaks along with the MgO substrate 111 and 222 peaks. Also visible are minute traces of the competing antiperovskite Mn_3GaC (111 peak at $2\theta \sim 40.0^\circ$ and 002 peak at $2\theta \sim 46.6^\circ$).

The expected epitaxial relationship for the Mn_2GaC film grown onto the MgO(111) surface is $[11\bar{2}0]_{\text{Mn}_2\text{GaC}} \parallel [10\bar{1}]_{\text{MgO}}$ in the film plane and $(0001)_{\text{Mn}_2\text{GaC}} \parallel (111)_{\text{MgO}}$ out of the plane. The inset in Figure 1 shows a pole figure at the $10\bar{1}3$ peak position ($2\theta = 41.89^\circ$, $\chi = 58.63^\circ$) displaying the sixfold symmetry of the film. Traces of the MgO 002 peak ($2\theta = 42.90^\circ$, $\chi = 54.47^\circ$) can also be seen confirming the epitaxial relationship. Furthermore, the a and c parameters obtained from XRD are 2.90 and 12.55 Å, respectively, compared with 2.90 and 12.49 Å for the calculated AFM[0001] $_2^4$ spin configuration.

Table 1. Identified set of most competing phases (cp) for $\text{Mn}_{n+1}\text{GaC}_n$ with corresponding formation enthalpy of the MAX phase, ΔH_{cp} , in meV/atom.

n	Set of most competing phases (cp)	ΔH_{cp} (meV/atom)
1	Mn_3GaC , C, MnGa_4	-30
2	Mn_2GaC , C, $\text{Mn}_{23}\text{Ga}_5$	+73
3	C, Mn_2GaC , $\text{Mn}_{23}\text{Ga}_6$	+137

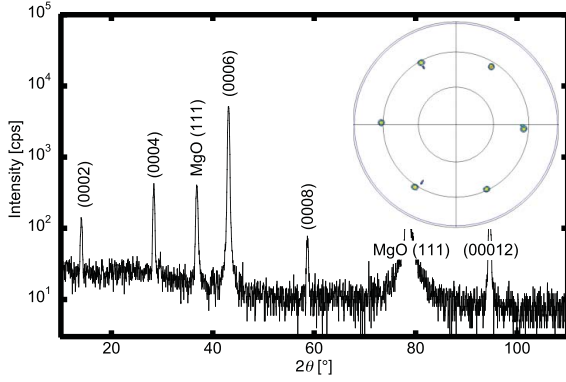


Figure 1. $\theta - 2\theta$ scan of the Mn_2GaC film demonstrating the high global structural quality of the film. The offset was decided by the film 0006 peak, so the MgO 111 substrate peak is severely reduced. The inset shows a pole figure at the 1013 peak position ($2\theta = 41.89^\circ$) displaying the crystal sixfold symmetry. Also seen in the pole figure are traces of the threefold symmetric MgO 002 peak, illustrating the epitaxial relationship between the substrate and the film.

The sample was prepared for cross-sectional (scanning) transmission electron microscopy, (S)TEM by conventional mechanical polishing and low-angle Ar-ion milling methods. High-resolution (HR) (S)TEM imaging was performed using the doubly corrected Linköping Titan, employing the embedded Super-X detector for energy dispersive X-ray (EDX) mapping. For elemental mapping, the respective K-lines were used. The low magnification (S)TEM image in Figure 2(a) shows a uniformly thick film (~ 100 nm), composed of grains of ~ 400 nm in width. The grains exhibit a homogeneous composition as shown by the EDX maps in Figure 2(b). The relative composition of the film is 52 at% Mn, 23 at% Ga and 23 at% C, which was estimated by EDX (not shown). The high crystal quality and atomic structure are shown by the selected area electron diffraction pattern in Figure 2(c) and the HR(S)TEM images in Figure 2(d) and Figure 2(e) which describe the $11\bar{2}0$ zone axis by its layered structure and typical atomic arrangement.

The magnetic response of the sample was measured in a vibrating sample magnetometer (VSM) in the temperature range 50–250 K with the magnetic field applied both parallel and perpendicular to the film plane. The in-plane low field response is shown in the main graph of Figure 3. A clear magnetic hysteresis is observed for temperatures up to and including 230 K, demonstrating that the film is FM in this temperature range. At 50 K, the saturation moment (at 5 T) is $m_s = 0.29 \mu\text{B}$ per Mn atom and the remanent moment is $m_r = 0.15 \mu\text{B}$ per Mn atom. The coercive field is found to be $H_c = 9$ mT, irrespective of temperature. With the field applied perpendicular to the film plane, the magnetic response is slowly varying with no remanence or coercivity observed, as shown in the inset of Figure 3. This means that the magnetic easy

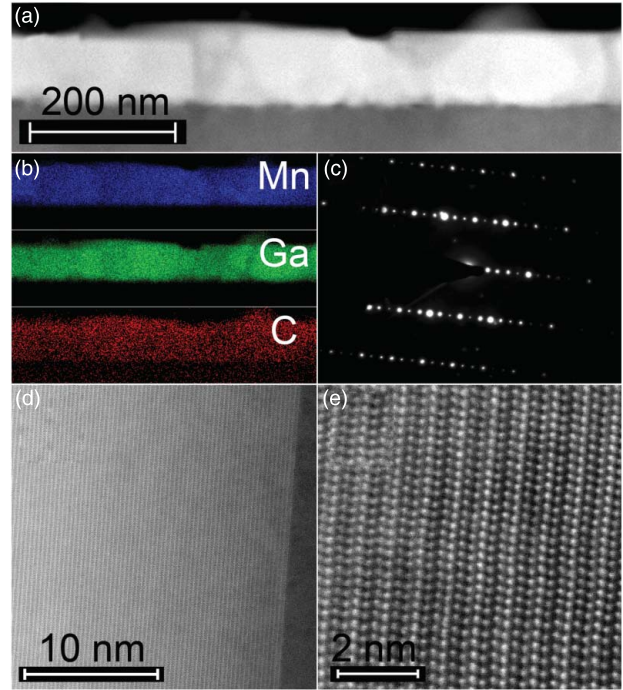


Figure 2. (a) Low magnification cross-sectional (S)TEM image of the film with (b) Mn, Ga and C elemental maps; (c) is a $11\bar{2}0$ zone axis selected area electron diffraction pattern while (d) and (e) are HR(S)TEM images of the structure (rotated).

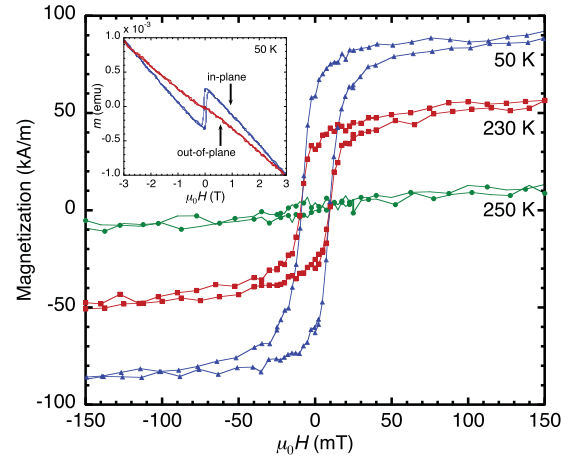


Figure 3. The low field magnetization measured with VSM for three different temperatures. A FM response is seen up to and including $T = 230$ K. The diamagnetic response of the substrate has been subtracted. Inset: The in-plane and out-of-plane magnetic moment m at 50 K, including the diamagnetic contribution from the substrate. An in-plane magnetic easy axis is observed.

axis lies in the film plane, which is typical of thin FM films where the shape anisotropy is the dominant term in the anisotropy energy.

Although a clear magnetic response is observed, the moment measured at 5 T is substantially lower than the magnitude of the theoretically calculated local Mn

moment which is close to $1.6 \mu\text{B}/\text{Mn}$ atom. This suggests that the observed ordering is in fact more complex than that of an ideal ferromagnet, where all Mn moments would be parallel at a field of 5 T. A variety of non-collinear or ferrimagnetic arrangements could account for this discrepancy. Indeed, complex non-collinear magnetic orders have been observed in other cases where, like in the present work, FM and AFM states are found to be close in energy, such as in FeNi invar alloys.[22] Pure Mn also displays a complex magnetic ground state.[23] It should be noted that the minute traces of antiperovskite Mn_3GaC detected in XRD analysis can be discarded as the origin of these magnetic characteristics, based on literature [24,25] as well as reference measurements on intentionally synthesized Mn_3GaC samples (unpublished).

These results confirm the strength of our predictive theory, not only through the discovery of a new member of the MAX phase family, but also by advancing beyond traditional MAX phase elements with Mn as the sole M element. This could spark a search for other unexplored MAX phases both with Mn as well as other metals previously not used for MAX phase synthesis. We further illustrate the possibility to employ MSE to deposit epitaxial thin films of phases containing Ga from elemental targets, allowing for improved process control as compared with bulk methods or methods that involve composite targets.

The magnetic measurements show a FM response in the temperature range from 50 to 230 K whereafter there is a sharp transition to an ordering that displays no remanance. This could indicate that the phase belongs to a family of materials that undergo a first-order magnetic transition that may be driven by temperature, or magnetic field. These transitions can, at least in part, be explained by the degeneracy in stability of different magnetic orderings, such as indicated by our calculations. Materials that display such sharp transition are of high interest, and known to display the magnetocaloric effect, allowing for possible use in efficient refrigeration technologies.[26,27] Knowing that the competing Mn_3GaC belongs to this group of materials [24,28–30] warrants a closer study of the magnetic properties of Mn_2GaC , although this is beyond the scope of the present study.

In conclusion, a new member of the MAX phase family has been discovered. Predicted through *ab initio* calculations, this phase is the first to contain Mn as the exclusive M element. The phase was synthesized as a heteroepitaxial thin film and was found to be FM up to 230 K, a temperature at which a sharp transition to a different magnetic ordering could be observed.

Supplementary online material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2013.865105>

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