Mn$_3$GaC inverse perovskite thin films by magnetron sputtering from elemental targets

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Keywords: inverse perovskite, magnetism, first principles calculations, thin films, magnetic ground state

Abstract
We have deposited epitaxial thin films of the inverse perovskite Mn$_3$GaC using magnetron sputtering from elemental targets. Two substrates were used, MgO (111) and (100), resulting in corresponding orientation of the Mn$_3$GaC thin films. Both samples displayed magnetic properties consistent with an AFM to FM transition at $\sim$170 K and a Curie temperature around 265 K, evaluated with vibrating sample magnetometry (in-plane measurements). These two ground states are further supported by first principles calculations. Based on that the two orientations of Mn$_3$GaC display very similar magnetic properties, it can be concluded that shape anisotropy dominates over the material’s easy axis.

Introduction

The Mn$_3$GaC inverse perovskite is an intermetallic material that undergoes a second order magnetic transition from paramagnetic (PM) to ferromagnetic (FM) state with Curie temperature at $T_C = 250$ K, then from ferromagnetic (FM) to an intermediate phase at 164 K, and a first order magnetic transition from intermediate phase to an antiferromagnetic (AFM) state with transition temperature $T_{t1} = 160$ K that can be induced by either temperature, pressure or magnetic field [1]. Driven by the temperature alone, this transition is followed by discontinuous change in volume of $\sim$0.5% [2]. The existence of an intermediate state between the FM and AFM states is probably due to carbon vacancies, as this is not observed in stoichiometric samples [3]. Furthermore, the material exhibits giant magnetoresistance [4] and a large magnetocaloric effect [5, 6], which makes it attractive from an application point of view.

In the antiferromagnetic state, the material is described as alternating ferromagnetic planes of Mn spins in the [111] direction, as determined by neutron diffraction, and with the moments in the AFM state being higher compared to the FM state [7, 8].

Previous first-principles theoretical investigations on Mn$_3$GaC [9] were performed more than 20 years ago, and it was then concluded that the ground state is the FM state, contrary to experimental observations suggesting that AFM is the ground state at $T = 0$ K. No recent first-principles calculations investigating different magnetic states can be found in the literature.

Generally, studies of this material are performed on powders [1] and polycrystalline samples [6] and to date there is only one report available showing thin film synthesis of Mn$_3$GaC [10]. The latter sample was grown from a polycrystalline target by pulsed laser deposition (PLD). This method may, however, exhibit challenges with respect to control of stoichiometry in the film growth [11, 12]. Furthermore, physical vapor deposition (PVD) synthesis from elemental targets in materials systems including Ga is challenging due to the low melting temperature ($T = 30^\circ$C), and hence no such depositions of Mn$_3$GaC has previously been reported. Still, a synthesis approach has been developed involving liquid Ga sputtering targets, initially for growth of GaN [13, 14] but thereafter also used for synthesis of Ga-based ternary carbides [15, 16].

Mn$_3$GaC is known to have its magnetic easy axis is along the (111) direction [8]. However, due to the very limited literature on related thin film growth, there are no studies targeting thin films of different specific...
crystallographic orientation, potentially demonstrating magnetization anisotropy. Such a study is highly motivated due to the competing effects between shape anisotropy and the magnetic easy axis.

In the present study, we have performed first-principles calculations on Mn$_3$GaC for evaluation of different magnetic spin configurations. We have also used magnetron sputtering to deposit Mn$_3$GaC thin films with different major crystallographic orientation, for subsequent magnetic characterization. We identify theoretical magnetic ground states consistent with known experimental data, and from magnetic characterization we find that the shape anisotropy dominates the measured magnetic characteristics.

**Experimental and computational details**

Calculations were performed using the projector augmented-wave (PAW) method [17] as implemented within the Vienna ab-initio simulation package (VASP) [18, 19]. Exchange and correlation effects were treated in the framework of the Perdew–Burke–Ernzerhof (PBE) [20] generalized gradient approximation (GGA) in its spin-polarized form. A plane wave energy cutoff of 400 eV was used, and sampling of the Brillouin zone was done using the Monkhorst-Pack scheme [21] with $22 \times 22 \times 22$, $12 \times 12 \times 12$ and $4 \times 4 \times 4$ k-point mesh for $1 \times 1 \times 1$, $2 \times 2 \times 2$ and $4 \times 4 \times 4$ for $4 \times 4 \times 2$ unit cells, respectively. To find the optimal structure for each phase, optimization of the geometry, atomic coordinates, volume, and shape of unit cell was performed.

In the FM state, all Mn spins were oriented in the same direction. For an AFM state, 5 different collinear and 1 non-collinear configurations were considered. A $2 \times 2 \times 2$ supercell was used to model the antiferromagnetic state, where ferromagnetic planes of Mn spins alternate in [111] direction, as described in [8], denoted as AFM-111. Figure 1 shows the schematic structure of perovskite Mn$_3$GaC in the FM and AFM-111 magnetic configuration. A non-collinear antiferromagnetic structure was modelled as described in [22] corresponding to the ground state of Mn$_3$GaN (denoted as NCL). Three other AFM configurations were modelled, with alternating spins within the same plane, however all these configurations relaxed to a non-magnetic (NM) state, and they were therefore not considered further. A model of the paramagnetic (PM) state was made using the disorder local moment (DLM) method [23], for which a randomly distributed solid solution of 50% spin up and 50% spin down is formed on the Mn site by means of special quasirandom structures (SQS) method [24].

Mn$_3$GaC inverse perovskite thin films were deposited by magnetron sputter epitaxy (MSE) using three confocally placed elemental targets: Carbon (3 inch, 99.99% purity) and Manganese (3 inch, 99.95% purity) at a 35° angle with respect to substrate normal, and Gallium (2 inch) prepared according to details described in [15]. The base pressure in the deposition chamber was $< 5 \times 10^{-8}$ Torr, and the Ar pressure was 4.5 mTorr. The sputtering targets were operated in constant current mode and were set to calibrated deposition fluxes corresponding to a ratio of 3:1:1 for Mn, Ga, and C, respectively. The applied current was then fine-tuned to optimize the growth rate. Films were grown simultaneously on (111) and (100) oriented MgO single crystal substrates, which prior to deposition were cleaned in ultrasonic baths of acetone, ethanol and isopropanol for 10 min, and then kept at deposition temperature of 650 °C for 60 min to ensure uniform temperature.

**Figure 1.** Schematic representation of atoms in (a) a unit cell of Mn$_3$GaC in FM configuration, and (b) a $4 \times 4 \times 2$ supercell in AFM-111 magnetic configuration.
distribution and gas desorption. Films were deposited for 30 min, yielding a film thickness of approximately 100 nm.

The structural properties of the films were investigated through x-ray diffraction (XRD), using a standard \( \theta - 2\theta \) geometry in a Panalytical Empyrean MRD with Cu K\( \alpha \) radiation (\( \lambda = 1.54 \) Å). The magnetic response of the samples was measured in a vibrating sample magnetometer (VSM) in the temperature range 100–300 K. The temperature dependent magnetization measurements were performed by applying 1 T to the sample with the magnetic field applied parallel to the film plane, and with a cooling rate of approx. 1 K per minute. The magnetic moment was recorded with a rate of 1 s\(^{-1}\). Field sweeps at a constant temperature were performed by changing the strength of the applied magnetic field parallel to the film plane, and the full cycle (changing the magnetic field from 0 T to 5 T, then decreasing it to \(-5\) T and back to 0 T) was performed twice.

**Results and discussion**

Figure 2 shows the total energy as a function of volume for different magnetic configurations of Mn\(_3\)GaC. The energies are given relative to the minimum energy of the non-magnetic state \(E^{NM}_0\).

![Figure 2](image)

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**Results and discussion**

Figure 2 shows the total energy as a function of volume for the simulated different spin configurations specified above. The energy is expressed relative to the energy minimum of the NM state, \(E^{NM}_0\) expressed in meV/atom. The magnetic ground state is the AFM-111, with larger volume as compared to the FM state. The obtained lattice parameter is 3.841 Å and 3.816 Å for AFM-111 and FM states respectively, which are in good agreement with the values obtained experimentally, 3.8900 Å and 3.8835 Å\(^{25}\). The obtained magnetic moment is 1.7 and 1.4 \(\mu_B\)/Mn atom for the AFM and FM states respectively, which are in excellent agreement with results obtained from neutron diffraction, i.e. 1.8 ± 0.1 and 1.3 ± 0.1 \(\mu_B\)/Mn atom for AFM and FM states\(^{8}\). Furthermore, from figure 2 it can also be seen that the PM state, modeled by DLM, has a significantly lower energy than the NM state. Furthermore, the NCL magnetic state relaxes to a NM state at volumes <53 Å\(^3\)/f.u., however, at larger volumes, the magnetic moment is retained and the energy is lower than that of NM. Similar trends have been observed in other first-principles studies\(^{26}\) on magnetic states of Mn metal. Ranking the magnetic states in terms of energy, the AFM-111 is the ground state, FM is close though with an energy 3 meV/atom higher compared to AFM-111, and the PM state (as modelled by DLM) correspondingly has an energy 15 meV/atom higher. Although the difference in energy between AFM and FM states is on the level of uncertainty of the calculations, this still illustrates a good agreement with the magnetic states experimentally observed in Mn\(_3\)GaC\(^{7,8}\) with an AFM state below 164 K, a FM state at temperatures between 164 K and 248 K, and a paramagnetic state above 248 K.

Figure 3 shows x-ray diffractograms of Mn\(_3\)GaC thin films deposited on MgO(100) (top) and MgO(111) (bottom) substrates. The former film displays only Mn\(_2\)GaC peaks, almost exclusively from a (100) preferential orientation, and with only minor amount of (111) oriented Mn\(_3\)GaC crystallites. The latter film (bottom scan) correspondingly display a preferred (111) orientation with only minor amount of (100) oriented crystallites. Trace amount of the nanolaminated Mn\(_2\)GaC is also present in this sample, marked with an asterisk. A \(\theta\) offset was set by the perovskite (111) peak, thus the intensity of the MgO(111) substrate peaks could be reduced. From
the XRD analysis, it can be concluded that the films are single phase with only negligible amount of secondary oriented grains.

Figure 4 shows the magnetization measured by applying the magnetic field parallel to the film plane as a function of temperature. The deposited Mn$_3$GaC thin films have a Curie temperature of $T_c = 265$ K and a transition between FM and AFM is also seen at around $T_t = 165$ K in the (100) oriented film and around $T_t = 170$ K in (111) oriented film. This shift in the transition temperature is most likely due to differences in strain in the films, as it is known that the Mn$_3$GaC transition temperature decreases under applied pressure [3]. According to the same reference, the Curie temperature increases with increased pressure, which can explain why the Curie temperature is higher than what is reported in the literature for bulk samples [27].

As seen in figure 5 from the field sweeps done at 300 K, there is still a ferromagnetic component at this temperature. Both samples show a similar magnetic response with no significant difference in magnetic behaviour. Considering that the magnetic properties of both samples were measured in-plane, it can be concluded that the shape anisotropy plays a key role, rather than the easy axis of the material.

Conclusions

We have performed ab-initio calculations for Mn$_3$GaC in different spin polarized magnetic states as well as for a simulated paramagnetic state. The identified ground states were found to be the AFM-111 orientation and FM,
with trends consistent with the experimentally observed magnetic states with respect to temperature. Thin films of inverse perovskite Mn₃GaC were grown on two different orientation of MgO substrates, 〈111〉 and 〈100〉, with most of the perovskite following the substrate orientation. The deposited films are under tensile stress, evident from the shift in Curie and Neél temperatures. As no significant differences were observed between the magnetic properties from the two different film orientations, we conclude that shape anisotropy is stronger than the material’s easy axis.

Acknowledgments

We acknowledge support from the Knut and Alice Wallenberg (KAW) Foundation for a Fellowship Grant and Project funding (KAW 2015.0043). The Swedish Research council is also gratefully acknowledged through Project 642-2013-8020. The calculations were carried out using supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC).

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Figure 5. Field sweeps done at 200 K and 300 K for samples with two different preferential crystal orientations, with the magnetic field applied parallel to the film plane. The cycle of varying the magnetic field strength was performed twice for each temperature and sample, and no noticeable hysteresis was seen in these cycles. The arrows point towards the respective scale of the respective sample, i.e. the sample with the (100) as a dominant orientation is plotted on the scale on the left side of the graph and the sample with the (111) as a dominant orientation is plotted on the scale on the right side of the graph.
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