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A magnetic atomic laminate from thin film synthesis: $(Mo_{0.5}Mn_{0.5})_2GaC$

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We present synthesis and characterization of a new magnetic atomic laminate: $(Mo_{0.5}Mn_{0.5})_2GaC$. High quality crystalline films were synthesized on MgO(111) substrates at a temperature of ~530 °C. The films display a magnetic response, evaluated by vibrating sample magnetometry, in a temperature range 3-300 K and in a field up to 5 T. The response ranges from ferromagnetic to paramagnetic with change in temperature, with an acquired 5T-moment and remanent moment at 3 K of 0.66 and 0.35 μ_B per metal atom (Mo and Mn), respectively. The remanent moment and the coercive field (0.06 T) exceed all values reported to date for the family of magnetic laminates based on so called MAX phases. [http://dx.doi.org/10.1063/1.4926611]

It has been five decades since the discovery of a new family of $M_{n+1}AX_n$ (MAX) compounds (n = 1-3)[1] composed of an early transition metal (M), an A group element (A), and carbon or nitrogen (X). The hexagonal structure is inherently atomically laminated and the stacking sequence for n = 1 is M-A-M-X-M-A-M-X-M along the c-direction. Due to a combination of metallic and covalent bonds, the materials display a unique combination of metallic and ceramic properties. Like metals, these phases exhibit good thermal and electrical conductivities and are easily machinable, and like ceramics, they are stiff, resistant to oxidation and thermal shock. To date, more than 70 MAX phases have been synthesized in thin film or bulk form.[2]

Alloying MAX-phases is a viable approach to alter specific properties, such as hardness in, e.g., $(Ti,V)_2AlC$,[3] $(V_{0.5}Cr_{0.5})_3AlC_2$, and $(V_{0.5}Cr_{0.5})_4AlC_3$[4] or (theoretically predicted) transport properties in, e.g., Ti_2AlC upon incorporation of oxygen.[5,6] More recently, alloying has been used for attaining the first magnetic MAX phases, through M-site alloying between Mn and Cr in $(Mn_xCr_{1-x})_2AlC$,[7–9] $(Mn_xCr_{1-x})_2GeC$,[10,11] and $(Mn_xCr_{1-x})_2GaC$.[12] Advancing beyond alloying, Mn_2GaC was recently theoretically predicted and subsequently synthesized as a heteroepitaxial thin film.[13,14] It should be noted that the sign of exchange coupling and thus the ground state (AFM or ferromagnetic (FM)) of Mn_2GaC can be tuned by changing the inter-layer distances,[15] which makes these systems extremely interesting for magnetocaloric[16] and spintronic[17] applications. In previously studied magnetic MAX phase alloys containing Cr and Mn, there is evidently an exchange interaction between Cr and Mn, which induces a change in net magnetization as well as transition temperatures with a change in the Cr to Mn ratio and choice of A element.[8–11,18] Alloying between Mn and another non-magnetic element would therefore likely affect the magnetic properties further and could serve to increase the understanding of this new class of materials.

Recently, thin film synthesis of epitaxial Mo_2GaC was reported. Characterization of the transport properties was consistent with previously predicted superconductivity of the phase.[19] The

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nonmagnetic nature of the compound along with the comparatively small formation enthalpy (−0.4 meV per atom) motivates alloying with Mn for introducing magnetism and for increasing the phase stability. In the present study, we perform thin film synthesis of $(Mo_{0.5}Mn_{0.5})_2GaC$ and investigate the magnetic properties. A new MAX phase alloy of high structural quality is presented, displaying a magnetic response up to at least 300 K.

Thin film deposition of $(Mo_{0.5}Mn_{0.5})_2GaC$ was performed using DC magnetron sputtering from two elemental targets of Ga and C together with a compound target composed of Mo and Mn with an atomic concentration ratio of 1:1. Previously developed procedures for sputtering from liquid targets (Ga) were employed.[20] Prior to deposition, the base pressure of the chamber was $3 \cdot 10^{-8}$ Torr and Ar was used as the sputtering gas at a pressure of 4.5 mTorr. Depositions were performed on MgO(111) substrates, which were ultrasonically cleaned in acetone, ethanol, and isopropanol each for 10 min. These were afterwards annealed in the synthesis chamber at the growth temperature for 15 min prior to deposition to remove surface contaminants and obtain a homogeneous temperature distribution. These parameters were obtained from a procedure for materials' optimization in line with previous work.[19]

Structural characterization of the thin films was performed through X-ray diffraction (XRD). The system utilized was a Panalytical Empyrean Materials Research Diffractometer (MRD) with a Cu k_α source. The measurements performed were symmetric (θ-2θ) scans obtained by employing a hybrid mirror and a 0.27° parallel plate collimator in the incident and the diffracted beam side, respectively. To study the elemental distribution in the film with atomic resolution, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) characterization and energy dispersive X-ray (EDX) mapping were carried out by using the Linköping double C_s corrected FEI Titan3 60-300 operated at 300 kV, equipped with the Super-X EDX system. A cross-sectional TEM-sample was prepared by conventional mechanical methods followed by a low angle ion milling and a fine polishing step with a low acceleration voltage of 1 keV. Overall, film composition was obtained using a scanning electron microscope (SEM) equipped with EDX. Magnetic measurements were performed utilizing a Vibrating Sample Magnetometer (VSM). The same magnetic measurements were performed on a MgO substrate for the background corrections of the magnetic response obtained from the films.

Synthesis of phase pure $(Mo_{0.5}Mn_{0.5})_2GaC$ thin films was accomplished at 530 °C on MgO(111) substrates. The XRD scan in Fig. 1 shows the diffraction peaks representing the basal planes (000*l*) of the film, indicating the epitaxial growth in a direction along the *c*-axis. The epitaxial relationship of the film and substrate in the in-plane and out-of-plane directions is $(Mo_{0.5}Mn_{0.5})_2GaC$ $[11\bar{2}0]||MgO[10\bar{1}]$ and $(Mo_{0.5}Mn_{0.5})_2GaC$ $[0001]||MgO[111]$, respectively. The two peaks at 36.85° and 78.48° belong to the substrate (111) and (222) planes. The *c*-lattice parameter from XRD is determined to be ~13.0 Å, which is approximately in the middle between the values of Mo_2GaC

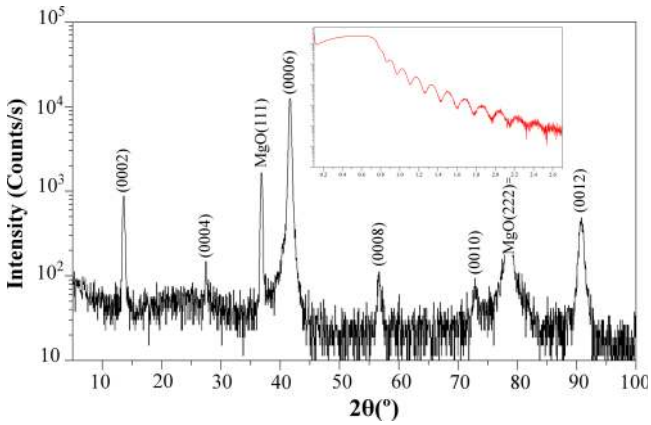

FIG. 1. θ-2θ x-ray scan of a $(Mo_{0.5}Mn_{0.5})_2GaC$ thin film grown on MgO(111) substrate. All the basal plane peaks of the MAX phase as well as the contribution of the substrate's crystal plane can be seen. The inset shows an XRR scan of the film where the film thickness could be estimated to ~50 nm.

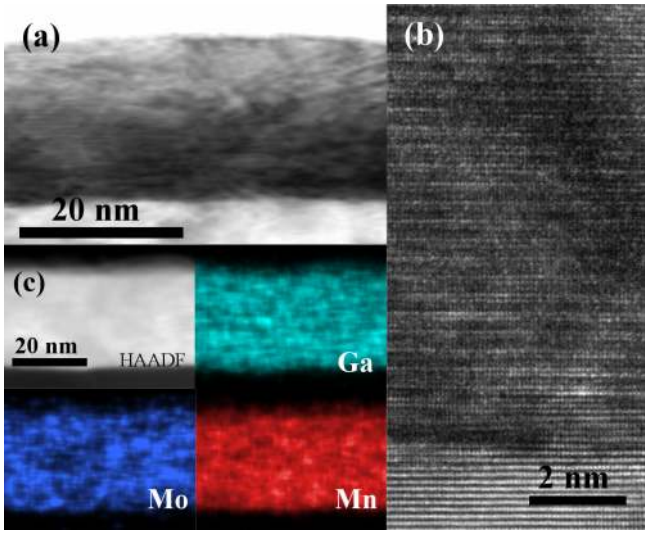

FIG. 2. (a) An overview TEM image of a 50 nm thick $(Mo_{0.5}Mn_{0.5})_2GaC$ film (top) and substrate (bottom), (b) high magnification micrograph showing the epitaxially growth of the film on the MgO(111) substrate, (c) HAADF image of the film with EDX mapping of Mo, Ga, and Mn, revealing the homogenous distributions of these elements within the film.

(13.43 Å)[19] and Mn_2GaC (12.55 Å),[13] consistent with what one might expect from Vegard's law[21] for a composition of $(Mo_{0.5}Mn_{0.5})_2GaC$. There is no indication of other crystalline phases or impurities in the XRD scan. The inset in Fig. 1 shows x-ray reflectivity (XRR) data, indicating a smooth film surface. Further, using XRR data, the thickness of the film was determined to be ~50 nm.

Additional structural characterization and compositional analysis from STEM/EDX are shown in Fig. 2. An overview image of the substrate (bottom) and the film (top) is shown in (a). In (b), a higher magnification micrograph demonstrates the epitaxial film growth and a smooth interface, while (c) shows a HAADF image from the part of the film where the EDX elemental mapping of Mo, Ga, and Mn was performed, revealing the homogeneous elemental distribution within the film, with no signs of clustering of Mn atoms. Measurements of the relative film composition revealed 34.8, 33.6, and 31.6 atomic percent for Mn, Mo, and Ga, respectively (with an estimated error bar of maximum 4 at. %), confirming the 2:1 ratio of M and A elements in the MAX phase in addition to a 1:1 ratio of the Mo and Mn atoms, consistent with the compound target composition used for the synthesis.

A high resolution micrograph is shown in Fig. 3(a) in addition to lattice resolved elemental mapping of Mn, Ga, and Mo in the film. These images clearly show well-defined Ga layers and a solid solution of Mo and Mn in the M layers. This is further confirmed by an EDX line profile across the layers.

The in-plane magnetic response of a thicker film (~450 nm) was measured using VSM in the temperature range 3 to 300 K and in a field up to 5 T. The magnetization presented in Fig. 4 reveals a FM response, as illustrated by the remanence, up to a temperature of 150 K. This is more clearly shown in the bottom-right inset image. The coercive field, H_c, for the film obtained at 3 K is determined to be 0.06 T, the largest value observed for any MAX phase to date.

Above the hysteretic region, the magnetization continues to increase with increasing field and does not saturate, even at the highest applied field (5 T). A high saturation field can be a signature of a large random anisotropy due to variations in the alignment of microcrystalline grains but this is not consistent with the high epitaxial quality of the films.

To examine this further, we investigate the remanent magnetization m_r and moment at the maximum available field of 5 T, m_{5T}. The resulting data are shown as a function of temperature in the top-left inset image of Fig. 4 in units of Bohr magnetons (μ_B) per metal atom (M). The values of m_r and m_{5T} at 3 K are approximately 0.35 and 0.66 μ_B per M-atom, respectively. This is the highest remanent moment measured for any magnetic MAX phase studied to date.[8,10–15,18] The second largest remanence, m_r, is found in the Mn_2GaC system, with ~0.3 μ_B per Mn atom at 3 K.[14] If the remanence of $(Mo_{0.5}Mn_{0.5})_2GaC$ is attributed to the Mn atoms only, this implies a value of $m_r \sim 0.7$ μ_B per Mn atom and an increase of the Mn remanence of about 130% compared to pure Mn_2GaC. However,

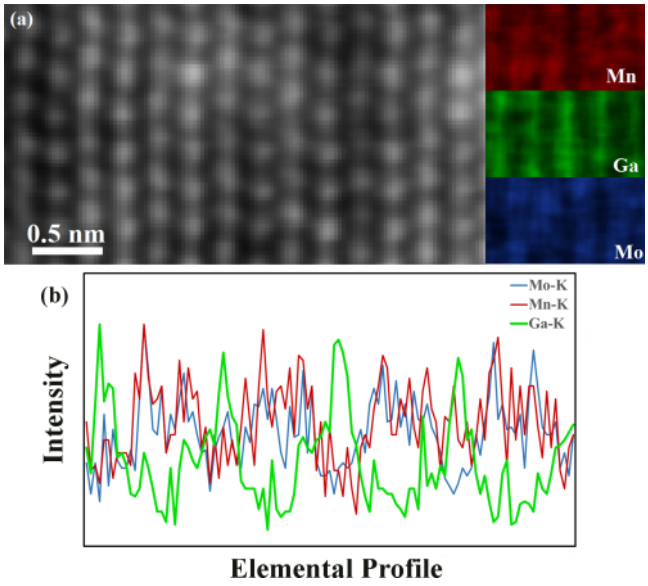

FIG. 3. (a) HR(S)TEM image and corresponding lattice resolved elemental mapping of Mn, Ga, and Mo and (b) EDX elemental line profile revealing the distribution of these elements within the selected area.

despite the paramagnetic nature of pure Mo,[19] no details of the individual moments of Mo/Mn can be concluded at this stage. That Mn may influence the moments of the Mo and Ga atoms cannot be ignored, which of course might affect the total magnetic response. For $(Mo_{0.5}Mn_{0.5})_2GaC$, both m_r and m_{5T} decay gradually with increasing temperature and the remanent moment disappears at around 150 K whereas a significant 5 T moment remains up to room temperature. The remanent magnetization indicates a FM component; however, the magnetization does not follow the $(T_c - T)^{\beta}$ temperature dependence characteristic of ferromagnets. Instead, the decaying remanence, without a clear ferromagnetic-paramagnetic phase transition, suggests a non-collinear magnetic state with a ferromagnetic component, which decreases with increasing temperature. More complex magnetic ordering than collinear ferromagnetism is further supported by previous studies of other magnetic MAX phases: Mn_2GaC,[13,14] $(Mn_{0.25}Cr_{0.75})_2GeC$,[10] and $(Mn_{0.5}Cr_{0.5})_2GaC$,[12] which indicated close to

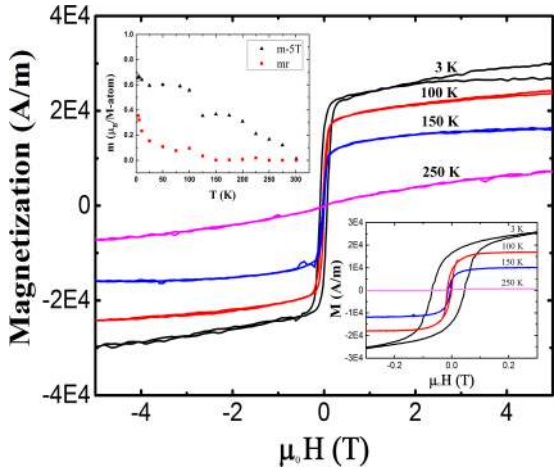

FIG. 4. High field magnetization from VSM analysis for four different temperatures measured up to 5 T magnetic field. The bottom-right inset shows the response in smaller field for the same temperatures. The coercive field is about 0.06 T at 3 K. The top-left inset shows the temperature dependence of the 5 T and the remanent magnetization. The remanent moment at 3 K is about 0.35 μ_B per M-atom, and the 5 T magnetization is about 0.66 μ_B per M-atom.

degenerate FM/AFM magnetic ordering. The competition between the two may promote a variety of non-collinear spin configurations, with or without remanent magnetization, which is consistent with a gradual transition from a more FM-like state at low temperatures to a state with high susceptibility (0.012 for $(Mo_{0.5}Mn_{0.5})_2GaC$) but no remanence at room temperature.

Comparing net magnetization and m_{5T} of the Mn_2GaC phase (1.7 μ_B per Mn atom)[14] and the present $(Mo_{0.5}Mn_{0.5})_2GaC$ films (0.66 μ_B per *M* atom, with implied potential 1.32 μ_B per Mn atom) at 3 K does not exclude comparable magnetic behaviour with the origin of the magnetism being the Mn-Mn exchange interaction. The fact that m_{5T} for $(Mo_{0.5}Mn_{0.5})_2GaC$ is lower than for Mn_2GaC might then suggest a weaker Mn-Mn exchange coupling due to a lower Mn concentration with resulting increased Mn-Mn distance. Itinerant magnetism has been suggested by Liu *et al.*[22] for $(Cr_{1-x}Mn_x)_2GeC$, $(0 \leq x \leq 0.25)$. The magnetization results presented here can neither confirm nor exclude the possibility of itinerant magnetic behavior for $(Mo,Mn)_2GaC$.

In conclusion, thin films of $(Mo_{0.5}Mn_{0.5})_2GaC$ were synthesized from magnetron sputtering at a temperature of 530 °C. Structural characterization reveals a phase pure film composed of epitaxially grown MAX phase. The films display a magnetic response throughout the investigated temperature range of 3-300 K, with a remanent magnetization of 0.35 μ_B per *M*-atom at 3 K, the largest reported remanence, and hence ferromagnetic response, of all known magnetic MAX phases to date. Above 150 K, the film displays no remanent magnetization, although a significant moment is observed in a field of 5 T, up to at least room temperature. The magnetic response may be explained by competing non-collinear FM and AFM ordering.

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