Magnetic Self-Organized Atomic Laminate from First Principles and Thin Film Synthesis

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The first experimental realization of a magnetic $M_{n+1}AX_n$ (MAX) phase, $(Cr_{0.75}Mn_{0.25})_2GeC$, is presented, synthesized as a heteroepitaxial single crystal thin film, exhibiting excellent structural quality. This self-organized atomic laminate is based on the well-known Cr₂GeC, with Mn, a new element in MAX phase research, substituting Cr. The compound was predicted using first-principles calculations, from which a variety of magnetic behavior is envisaged, depending on the Mn concentration and Cr/Mn atomic configuration within the sublattice. The analyzed thin films display a magnetic signal at room temperature.

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Layered magnetic materials are fascinating from the point of view of fundamental science as well as applications. Discoveries such as giant magnetoresistance [1,2] in magnetic multilayers [3] have revolutionized data storage and magnetic recording, and concurrently initiated the search for new layered magnetic materials. One group of inherently nanolaminated compounds are the so-called $M_{n+1}AX_n$ (MAX) phases [4]. MAX phases are based on a transition metal (M), an A-group element (A), and carbon or nitrogen (X), with the different elements forming individual atomic layers [4]. The structure is hexagonal with a repeated M-A-M-X-M-A-M-X atomic layer stacking in the c direction (see Fig. S1 in the Supplemental Material [5]).

MAX phases have attracted considerable interest due to unique material properties combining the characteristics of metals and ceramics, and the large number of isostructural compositions. Around 60 phases [6] have been synthesized in bulk or thin film form from combinations of M, A, and Xelements. Investigated properties include, e.g., reversible deformation [7] and stability of nanosheets upon exfoliation [8]. In addition, anisotropic optical and electronic properties are predicted [9,10], including tunable conductivity in the c direction [11].

Magnetism combined with the nanolaminated structure characterized by high stability and tunable anisotropic properties can potentially allow the fabrication of functional MAX phases for various applications in spintronics. The existence of ferromagnetism in MAX phases has not previously been demonstrated experimentally, although predicted by theory [12–14]. Antiferromagnetic (AFM) spin ordering has also been suggested based on an adjustable *U* formalism [15–17]. In the present work, we report on a prediction through *ab initio* calculations of a stable magnetic MAX phase, $(Cr_{1-x}Mn_x)_2GeC$, with ferromagnetic (FM) or antiferromagnetic ordering depending on the Cr/Mn intermixing within the *M* sublattice. This is followed by a successful experimental synthesis of a magnetic $(Cr_{0.75}Mn_{0.25})_2$ GeC alloy exhibiting a magnetic signal at room temperature. The experimental results therefore verify the existence of a new structurally stable magnetic MAX phase.

As a starting point the stability of $(Cr_{1-x}Mn_x)_{n+1}GeC_n$ phases with respect to all competing phases was theoretically evaluated (see Supplemental Material [5]). $Cr_2GeC (x = 0)$ was identified as a stable phase, in accordance with experimental observations, with exothermic formation enthalpy $\Delta H_{cp} = -1$ meV/atom when in its lowest energy (antiferromagnetic) configuration. The pure Mn (x = 1) MAX phase was found to be unstable, with a ΔH_{cp} of 30 meV/atom. Analysis of the magnetic moment m_M in μ_B per M atom in the FM configuration shows that Cr_2GeC has $m_M = 0$, in agreement with experimental observations. For the unstable Mn₂GeC, the magnetic moment is, however, significant with m_M of 2.0. Based on these observations, we concentrated the theoretical work on stability and magnetic properties of a mixture of Cr and Mn on the M sublattice in the alloy $(Cr_{1-x}Mn_x)_2$ GeC. The alloy has been modeled using several ordered as well as disordered atomic configurations, the latter using the special quasirandom structure method (SQS) [18]. The structures have been studied in different magnetic states, including nonmagnetic, FM, various AFM, double-layer antiferromagnetic (DAFM), and paramagnetic modeled with disordered local moments [19]. It should be noted that, even though several ordered and disordered atomic configurations have been considered for both x = 0.25 and x = 0.50 superstructures, those with pure Mn-C-Mn layers (see Fig. S2 in [5]) are found to have the lowest energy, in accordance with the A = Al alloy [14].

The magnetic ground state of these ordered configurations is degenerate FM or DAFM, see squares and triangles

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in Fig. 1(a), where the latter consists of ferromagnetically ordered Mn-C-Mn layers where the order between two such Mn double layers is antiparallel, with a resulting global AFM state.

Our calculations, used both to predict phase stability and to explain experimental observations, show that MAX phase stability is mainly governed by the enthalpy term in the Gibbs free energy [14,20]. However, for borderline cases, entropy and vibrational effects will come into play at elevated temperatures. Evaluation of configurational entropy for $(Cr_{1-x}Mn_x)_2$ GeC with atomically disordered Cr/Mn configurations is therefore presented in Fig. 1(a), through the formation free energy $\Delta G_{\rm FM}$ of FM $(Cr_{1-x}Mn_x)_2$ GeC relative to FM Cr₂GeC (x = 0), displayed for temperatures between 0 and 1200 K in steps of 300 K. The energy of the ordered superstructure with lowest energy, shown with open symbols in Fig. 1(a), is lower as compared to the atomically disordered structure at 0 K (the top curve). However, at, for example, x = 0.25, the entropy originating from disorder in M elements makes the solid solution more favorable with respect to ordered configurations already around 600 K, and the alloy becomes thermodynamically stable with respect to decomposition into other competing phases around 900 K. Evaluating different magnetic states of the disordered configurations for x = 0.25 and 0.50 (not displayed in the figure), the energies of various AFM configurations are around or above the FM states displayed in the graph. Furthermore, disordered local moment magnetic configurations representing the paramagnetic states are well above the lowest energy magnetic state for ordered as well as disordered atomic configurations. The local magnetic moments of Cr and Mn in the $(Cr_{0.75}Mn_{0.25})_2$ GeC SQS cell are given in Fig. 1(b) sorted by size in one FM and one AFM configuration. The Mn moments are robust regardless of configuration with a magnitude around



FIG. 1 (color online). Theoretical analysis of relative stability and magnetic properties of $(Cr_{1-x}Mn_x)_2GeC$. (a) Formation energy ΔG_{FM} of $(Cr_{1-x}Mn_x)_2GeC$ relative to FM Cr₂GeC (x = 0.00), for x = 0.00, 0.25, and 0.50. Filled symbols represent disordered Cr and Mn configurations, and open symbols correspond to ordered configurations. (b) Calculated local magnetic moments of Cr and Mn atoms at x = 0.25 with FM and AFM order.

 $2\mu_B$. The magnitude of the Cr moments varies between 0 and $1.5\mu_B$ depending on the configuration, adapting to the general direction of neighboring Mn moments.

Our theoretical predictions suggest that alloying of Cr and Mn is a viable strategy to obtain a stable magnetic MAX phase. We therefore synthesized epitaxial $(Cr_{0.75}Mn_{0.25})_2$ GeC MAX phase films by UHV magnetron sputtering, using three confocal sources: C, Ge, and $Cr_{75\%}/Mn_{25\%}$, at a deposition temperature of 600 °C on MgO(111) substrates (see Supplemental Material [5]). Structural characterization using x-ray diffraction and reflection (XRR) is shown in Fig. 2. The most notable peaks in the x-ray diffraction data, other than from the MgO substrate, are the basal peaks of the MAX phase. Also visible is the Ge (111) peak originating from excess Ge clusters on the surface of the film [21]. No indications of the presence of the other competing crystalline phases were observed. The inset in Fig. 2 shows the XRR data (circles) along with a single layer model fit which demonstrates that the MAX phase film is a well-defined single layer of thickness 36.1 ± 0.4 nm. Additionally, the asymmetric (103) plane spacing as the in-plane (110) was measured and compared to calculations. A deviation of less than 1% was found [2.16 versus 2.15 Å for (103), 1.48 versus 1.47 Å for (110), and 2.02 versus 2.00 Å for (006)]. The (103) spacing was identical to experimental data on pure Cr₂GeC, while the (006) spacing was 0.3% larger. The measured lattice parameters are then for the present film a = 2.95 Å and c = 12.11 Å.

Structural as well as composition characterization was performed through aberration corrected (scanning)



FIG. 2 (color online). Global structural quality by x-ray diffraction. θ -2 θ scan of the $(Cr_{0.75}Mn_{0.25})_2$ GeC film grown on MgO(111). All peaks are identified as belonging to the MAX phase and substrate apart from a small peak at ~27° corresponding to Ge crystallites on the surface of the film. The inset shows the XRR data (open circles) along with the fitted curve (line) corresponding to a film thickness of 36.1 ± 0.4 nm. The roughness and density are estimated to be 1.3 ± 0.2 nm and 6.8 ± 0.3 g/cm³, respectively.

transmission electron microscopy [(S)TEM] (see Supplemental Material [5]). Figure 3(a) is a low magnification, high contrast image of the film (middle) and substrate (bottom). The film exhibits a uniform thickness of \sim 36 nm and is exclusively composed of epitaxially grown MAX phase, consistent with the x-ray analysis. The high quality nanolaminated structure is illustrated in Fig. 3(b), which shows a lattice image of the film, with alternating two bright M layers with one darker A layer. To explore the compositional uniformity of the film, the M elements Cr and Mn along with the A element Ge were mapped in a region of the film, as shown by the high angle annular dark field (HAADF) image in Fig. 3(c). The energy dispersive x-ray spectroscopy (EDX) Ge-L, Cr-K, and Mn-K edges were used for elemental mapping as shown in Figs. 3(d)-3(f), respectively. The Cr- K_{β} and Mn- K_{α} peaks are overlapping, so in order to map Cr and Mn exclusively, $\operatorname{Cr} K_{\alpha}$ and $\operatorname{Mn} K_{\beta}$ were used.

Since the latter edge is rather weak, the corresponding map suffers from noise. Regardless, the mapping reveals a mixing of all three elements with no indication of segregation across the film. Finally, Fig. 3(g) shows an EDX spectrum obtained by averaging the film spectrum image, which apart from the indicated elements also reveals the *X* element C, as well as Ti, which is a residue from the TEM sample preparation process. The three elements Ge, Cr,



FIG. 3 (color online). Local structural quality and composition. Low magnification (S)TEM EDX imaging of the film. (a) A low magnification, high contrast image of the film (middle) and substrate (bottom). (b) A lattice image of the film, alternating two bright *M* layers with one darker *A* layer. The HAADF image showing the composition uniformity of the film is shown in (c). The EDX Ge-*L*, Cr-*K*, and Mn-*K* edges were used for elemental mapping as shown in (d)–(f) respectively. Finally, (g) shows an EDX spectrum obtained by scanning the beam in the film area, which apart from the indicated elements also reveals the *X* element C and Ti, which is a residue from the sample preparation process (the sample is mounted in a Ti grid).

and Mn are relatively quantified in the following relation: 28.8:53.6:17.6, with a Cr:Mn ratio close to 3:1, corresponding to x = 0.25 in the $(Cr_{1-x}Mn_x)_2$ GeC notation.

Figure 4 contains the results from a high resolution (S)TEM study of the film, with a HR(S)TEM image and corresponding fast Fourier transform (FFT) in Figs. 4(a) and 4(b), respectively. The contrast is exclusively mass related, and the heavier A layer appears with increased contrast with respect to the two darker M layers. Figures 4(c) and 4(d)contain the results from a high resolution EDX map, where Fig. 4(c) is a 256×256 pixel STEM image of the mapped area from 4(a) and 4(d) shows the corresponding Cr-K, Mn-K, and Ge-K elemental maps. In Fig. 4(d), the elementally laminated structure is instructively exemplified. The mixing of the Cr and Mn elements in the Mlayer is apparent, as is the identification of Ge as the A layer. Finally, Fig. 4(e) shows an averaged line profile across the layers. As seen in the figure, the layers are chemically well defined, forming a natural superlattice with a clearly defined period.

The magnetic response of the sample was measured in a vibrating sample magnetometer and the results are shown in Fig. 5. The film shows a magnetic response over the whole investigated range of temperatures. Almost no anisotropy is observed in the magnetization, as shown in the top-left inset in Fig. 5 where a small in-plane remanence is identified,



FIG. 4 (color online). Aberration corrected HR(S)TEM imaging and lattice resolved EDX elemental mapping of the MAX structure. The atomically resolved mass contrast image is shown in (a) with associated FFT in (b). The mapped area and Cr-K, Mn-K, and Ge-K lattice resolved elemental maps are seen in (c) and (d) with an averaged EDX line profile shown in (e).



FIG. 5 (color online). The magnetic response measured with a vibrating sample magnetometer for three different temperatures. A magnetic response is seen up to the maximum measurement temperature of T = 300 K. Top-left inset: The in-plane and out-of-plane magnetization M for low applied field at 50 K, from which the in-plane coercive field was determined to be 28 ± 5 mT. A small remanence is seen in the in-plane orientation. Bottom-right inset: The temperature dependence of the saturation moment m_s , including a fit to the functional form $1-\alpha T^{\beta}$, and the remanent moment m_r in units of the Bohr magneton per Mn atom.

while no out-of-plane remanence can be unambiguously resolved. The temperature dependence of the saturation moment m_s (in a field of 4 T) and the remanent moment m_r are shown in the bottom-right inset. The saturation moment decreases with temperature and can be fitted at low temperature by the functional form $m_s(T)/m_s(0) =$ $1 - \alpha T^{\beta}$, with $\beta = 3/2$, which is consistent with Bloch's law. The saturation moment at 50 K is $0.36 \pm 0.03 \mu_B$ per Mn atom whereas the remanence is $0.031 \pm 0.006 \mu_B$ per Mn atom. The remanence decreases with temperature and above 200 K it is below the resolution limit. The saturation moment and remanent moment (per Mn atom) were found to be the same in a 102 nm thick film, demonstrating that the magnetic signal originates from the bulk of the film and not the interfaces.

The small in-plane field remanence shows that the magnetic coupling within the layers is partly ferromagnetic. However, the total remanence only accounts for one-tenth of the measured saturation moment, which in turn is only a fraction of what would be expected from a completely ferromagnetic ordering deduced from the calculated magnetic moments. These measurements therefore indicate the presence of competing magnetic interactions in the system, where antiferromagnetic coupling narrowly wins over ferromagnetic in most cases, but due to the small energy difference the ferromagnetic phase becomes favored under low applied fields. This could take place either on the level of local moments or on a larger length scale involving the coupling between layers or superparamagnetic regions. This interpretation is in line with our theoretical calculations where the energy differences for $(Cr_{0.75}Mn_{0.25})_2$ GeC show that AFM systems are just below FM ones in energy. However, the energy difference is on the order of 1 meV/atom, depending on the geometry of the SQS, which is within the uncertainty of the theoretical calculations. Furthermore, the details of the Cr/Mn configuration and small fluctuations in the local composition of all four elements are likely to influence the magnetic interactions in line with the findings of Dahlqvist *et al.* [14], so that the local variations of ordering tendency in the present case may lead to a span of magnetic order from barely ferromagnetic to more robust antiferromagnetic.

The complexity of the magnetic ordering in the layered Mn-containing MAX phase is not surprising when considering that monolayers or atomic chains of Mn can display intricate magnetic ordering such as chiral magnetic order [22,23] and other even more complex magnetic structures [24]. This delicate balance between AFM and FM states is actually of high interest for spintronic applications, as the electronic properties of such materials could be altered upon application of magnetic fields. In the films investigated here, the Cr/Mn configuration is most likely disordered, in accordance with the corresponding A = Al alloy [25]. By altering the concentration of the M elements within the MAX phase, or facilitating ordered configurations with complete Cr or Mn atomic layers, different magnetic ordering can be promoted. This allows the tuning of magnetic behavior, in contrast to the conventional approach of varying the interlayer thickness [3] or interface quality [26], for example.

In conclusion, predictions from first principles calculations combined with thin film synthesis and characterization reveal a new magnetic self-organized atomic laminate displaying a magnetic signal at room temperature. Taking advantage of the naturally layered structure of these materials and their highly anisotropic transport properties, which can additionally be tuned by *X*-element alloying [11], there is a great potential to use magnetic MAX phases for electronic and spintronic applications.

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