Theoretical Prediction and Experimental Verification of the Chemically Ordered Atomic-Laminate i-MAX Phases $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$

Andrejs Petruhins, Martin Dahlgqvist, Jun Lu, Lars Hultman and Johanna Rosén

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Theoretical prediction and experimental verification of the chemically-ordered atomic-laminate *i*-MAX phases $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$

A. Petruhins, M. Dahlqvist, J. Lu, L. Hultman, and J. Rosen

Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-581 83, Linköping, Sweden

Abstract

We combine predictive *ab-initio* calculations with verifying bulk materials synthesis for exploration of new and potentially magnetic atomically laminated *i*-MAX phases. Two such phases are discovered: $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$, where the latter compound displays a two-fold increase in Mn content compared to previously reported bulk MAX phases. Both new compounds exhibit the characteristic in-plane chemical order of Cr(Mn) and Sc, and crystallize in an orthorhombic structure, space group *Cmcm*, as confirmed by scanning transmission electron microscopy (STEM). From density functional theory (DFT) calculations of the magnetic ground state, including the electron-interaction parameter *U*, we suggest an antiferromagnetic ground state, close to degenerate with the ferromagnetic state.

I. INTRODUCTION

MAX phases are a group of ternary nanolaminated compounds consisting of a transition metal *M*, an A-group element *A* and carbon and/or nitrogen *X*, with general formula $M_{n+1}AX_n$ ($n = 1 - 3$) [1,2]. The total number of MAX phase family members is currently above 100. These materials are interesting due to their combination of metallic and ceramic properties, such as high electrical and thermal conductivity, good damage tolerance and ability to maintain strength at high temperatures [1,3]. Some phases are resistant to oxidation and corrosion [4], resistant to creep and fatigue [5], crack self-healing [6,7], and others are stable against neutron radiation [8,9].

In 2013, the first magnetic MAX phase was realized in thin film form by alloying Cr₂GeC with Mn [10]. This discovery was followed by other Mn-based materials, including (Cr,Mn)₂AlC [11], (Cr,Mn)₂GaC [12] and (Mo,Mn)₂GaC [13], see [14] and references therein. A prerequisite for the latter two materials was process developments based on magnetron sputtering from elemental (liquid) Ga targets [15]. This enabled synthesis of MAX phase thin films with Ga as an *A* element [13,16,17], and the discovery of Mn₂GaC [18], followed by (Cr_{1-x}Mn_x)₂GaC thin films over the whole composition range, $0 \leq x \leq 1$ [15,18,19], by virtue of quenching from the relatively low-temperature processing. However, further research indicated that the solubility limit of Mn in Cr₂AC (*A*= Ge, Al, and Ga) bulk synthesis is lower as compared to corresponding thin films. For example, in the (Cr_{1-x}Mn_x)₂GaC system, the highest Mn content shown in bulk material is $x = 0.3$ [20], although a composition of $x=0.5$ has been suggested based on initial elemental powder ratios [12]. It has been shown, however, that the Mn solubility in the MAX phase is typically lower than the initial powder composition [20]. To date, despite several attempts, there is no report on Mn₂GaC synthesis in bulk form.

Discoveries of new MAX phases and related hybrid materials have been achieved not only by exploration of new MAX phase elements, but also through new, chemically-ordered structures. Examples thereof are quaternary so called *o*-MAX phases, with out-of-plane chemical ordering based on alternating layers of different elements in a sandwich-like structure[21] and quaternary MAX phases coined *i*-MAX with in-plane chemical order in the *M* plane [22]. The main characteristics of the latter phases, of general formula $(M_{2/3}^1 M_{1/3}^2)_2 AX$, is the minority M^2 element extending from the plane of the majority M^1 element, towards the *A* layer. Furthermore, the *i*-MAX phases have been shown to form a family of materials, with novel compositions and Kagomélike ordering of the *A* layer, to date experimentally verified for (Mo_{2/3}Sc_{1/3})₂AlC [23], (Cr_{2/3}Sc_{1/3})₂AlC and (Cr_{2/3}Y_{1/3})₂AlC [24], (Mo_{2/3}Y_{1/3})₂AlC [22], (V_{2/3}Zr_{1/3})₂AlC [22], (W_{2/3}Sc_{1/3})₂AlC and (W_{2/3}Y_{1/3})₂AlC [25], (Cr_{2/3}Zr_{1/3})₂AlC [26], (Mo_{2/3}Sc_{1/3})₂GaC and (Mo_{2/3}Y_{1/3})₂GaC [27]. Furthermore, 11 *i*-MAX phases including rare earth (RE) elements, (Mo_{2/3}RE_{1/3})₂AlC were most recently reported [28], displaying a multitude of magnetic characteristics, though with transition temperatures typically below 30 K. This is in contrast to previous Mn-based MAX phases, Mn₂GaC and (Mn_{0.5}Cr_{0.5})₂GaC, which have shown transition temperatures in a range up to ~500 K [29,30]. At present there is no Mn-based magnetic *i*-MAX phase, though this would be highly interesting, as chemical ordering of magnetic elements in a material stands at the crossroads of fascinating condensed matter physics[31,32], and since such compounds may realize higher Neel/Curie temperatures.

In a quest for novel magnetic *i*-MAX phases, we here report on a theoretical-experimental approach to investigate potential formation of *i*-MAX phases based on Cr and Mn. We combine theoretical predictions of phase stability and magnetic ordering with (bulk) materials synthesis, targeting $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ *i*-MAX. Both phases are experimentally realized, verified through X-ray diffraction and transmission electron microscopy, and showing a significantly increased Mn content compared to other bulk MAX phase materials.

II. METHOD

A. Computational details

All first-principles calculations were based on density functional theory, and were performed with the Vienna *ab-initio* simulation package (VASP) [33-35] using the projector augmented wave method [36,37] with spin-polarized generalized gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE) [38] for treating electron exchange and correlation effects. Wave functions were expanded in plane waves up to an energy cutoff of 400 eV, and sampling of the Brillouin zone were done using the Monkhorst-Pack scheme [39]. In addition, we also used the rotationally invariant approach as proposed by Dudarev [40]. Note that within this formalism the onsite Coulomb parameter U and the exchange parameter J are spherically averaged into a single effective interaction parameter $U_{\text{eff}} = U - J$ that does not depend on their individual values. The equilibrium structures are obtained by minimization of the total energy with respect to volume and with full relaxation of atomic positions and unit cell parameters until forces are converged below 10^{-3} eV Å⁻¹.

So far, most *i*-MAX phases crystallize in the monoclinic $C2/c$ (#15)[23] and orthorhombic $Cmcm$ (#63)[22,24] structure. These structures are very similar, essentially degenerate in energy, but with a difference in their M_2C stacking [22]. Based on the experimental findings presented herein, we only use the $Cmcm$ structure for our theoretical survey of magnetic ground state. We have considered several collinear magnetic spin configurations for $(M_{2/3}^1\text{Sc}_{1/3})_2\text{GaC}$, $M^1 = \text{Cr}$ or Mn , using notations defined previously for magnetic M_2AX phases [41-43]. Figure 1 and Table I summarizes these notations and their respective spin direction at each M^1 site in the orthorhombic $Cmcm$ (#63) structure. For simplicity, we here introduce a shortened version for some of the notations; AFM1 = AFM[001]₁, X2 = AFM[001]₂^X, A2 = AFM[001]₂^A, and in-A = in-AFM (i.e. an in-plane ordered AFM spin configuration with two up and two down spins on

M^I in each layer). In addition, spin configurations with the same spin direction before changing sign upon crossing an X or A layer were considered; $X4 = \text{AFM}[001]_4^X$ and $A4 = \text{AFM}[001]_4^A$, using an extended $1 \times 1 \times 2$ unit cell. All considered spin configurations are visualized in Figure S1 (ref. [44])

Table I. Definition of the 10 magnetic spin configurations considered for $(M_{2/3}^I \text{Sc}_{1/3})_2 \text{GaC}$, where $M^I = \text{Cr}$ or Mn , within the Bravais unit cell of space group $Cmcm$ consisting of 48 atoms with 16 M^I sites.

Atom M^I	Direct coordinate			Spin configuration									
	x	y	z	FM	AFM1	X2	A2	in-A1	in-A2	in-A3	in-A4	in-A5	in-A6
M1	x	y	z	+	+	+	+	+	+	-	-	+	-
M2	-x	y	z	+	+	+	+	-	-	+	+	+	+
M3	x+1/2	y+1/2	z	+	+	+	+	+	+	-	-	-	+
M4	-x+1/2	y+1/2	z	+	+	+	+	-	-	+	+	-	-
M5	x	y	-z+1/2	+	-	+	-	+	-	+	-	+	-
M6	-x	y	-z+1/2	+	-	+	-	-	+	-	+	+	+
M7	x+1/2	y+1/2	-z+1/2	+	-	+	-	+	-	+	-	-	+
M8	-x+1/2	y+1/2	-z+1/2	+	-	+	-	-	+	-	+	-	-
M9	x	-y	z+1/2	+	+	-	-	-	-	-	-	+	-
M10	-x	-y	z+1/2	+	+	-	-	+	+	+	+	+	+
M11	x+1/2	-y+1/2	z+1/2	+	+	-	-	-	-	-	-	-	+
M12	-x+1/2	-y+1/2	z+1/2	+	+	-	-	+	+	+	+	-	-
M13	x	-y	-z	+	-	-	+	-	+	+	-	+	-
M14	-x	-y	-z	+	-	-	+	+	-	-	+	+	+
M15	x+1/2	-y+1/2	-z	+	-	-	+	-	+	+	-	-	+
M16	-x+1/2	-y+1/2	-z	+	-	-	+	+	-	-	+	-	-

Figure 1. Schematic representation of the orthorhombic $Cmcm$ $(M_{2/3}^{1/3}Sc_{1/3})_2GaC$ structure, $M^1 = Cr$ or Mn , along the (a) $[010]$ and (b) $[001]$ zone axes with enumeration of M^1 sites.

The thermodynamic stability was evaluated using a linear optimization procedure based on the simplex method, which compares the energy of the compound of interest to all possible linear combinations of other competing phases under the constraint of a fixed stoichiometry [45,46]. The linear combination of competing phases resulting in the lowest energy is called equilibrium simplex or set of most competing phases. A compound's stability can be quantified in terms of formation enthalpy ΔH_{cp} by comparing its energy to the energy of the equilibrium simplex, $\Delta H_{cp} = E(\text{compound}) - E(\text{equilibrium simplex})$. If $\Delta H_{cp} < 0$ the compound is considered stable, while for $\Delta H_{cp} > 0$ it is considered to be not stable or at best metastable. For compounds that are found here to be not stable, the equilibrium simplex indicates the combination of other phases being more stable. Competing phases included in the evaluation of phase stability are those experimentally known as well as hypothetical phases that exist in similar and/or with neighboring elements in the Periodic table of elements. A complete list of competing phases considered herein are given in Table SI in Supplemental Material (ref. [44]).

Temperature-dependent effects such as lattice vibrations were not considered, as such contribution from a phase, significant or not, tend to be cancelled out in the calculated stability [47]. This approach has been proven to work exceptionally well for both MAX [46,48,49] and *i*-MAX phases [22,23]. Schematics were produced with VESTA [50].

B. Materials synthesis

Polycrystalline samples of $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$ were synthesized by solid-state reaction from elemental constituents: elemental powders were used for Cr (99.5%, mesh -100, Sigma Aldrich), Mn (99.99%, Sigma Aldrich), Sc (99.99% (Sc/TREM), mesh -200, Stanford Advanced Materials) and graphite (briquetting grade, 99.9995%, -200 mesh, Alfa Aesar). For Ga, metal pellets (99.99999%, Mining and Chemical Products Limited) of about 7 mm diameter weighing ~ 1 g were used, which were further mechanically cleaved into smaller pieces of about 1 mm in size. For both $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$, Cr/Mn:Sc:Ga:C material (powders for Cr/Mn, Sc, and C and pellets for Ga) was prepared in a stoichiometric ratio of 4:2:3:3. First, Cr/Mn, Sc, and C powders were mechanically mixed in an agate mortar. The powder mixture was then placed in an alumina crucible, Ga pellets were added, and the

pellet/powder mixture was stirred. The alumina crucible with elemental constituent mixture was then heated under Ar flow to 1400 °C at a rate of 10 °C/min, and finally held at 1400 °C for 5 h.

C. Materials analyses

XRD analysis of powder samples were performed using Panalytical X'pert powder diffractometer using Cu K α radiation ($\lambda = 1.54$ Å) equipped with Bragg-Brentano HD on incident side with 1/4° divergence slit and 1/2° anti-scatter slit. On diffracted beam side, a 5-mm anti-scatter slit together with a Soller slit (with an opening radius of 0.04) was used. A continuous scan from 5° to 120° was performed on the sample with step size of 0.008° and counting time of 60 s per step.

Specimens for STEM analysis were prepared by dispersing powder on Cu grid with C film. STEM combined with high-angle annular dark-field imaging and EDX analysis with a Super-X EDX detector was performed in the double-corrected Linköping FEI Titan³ 60-300 operated at 300 kV.

III. RESULTS AND DISCUSSION

A. Stability predictions

In the evaluation of the theoretical phase stability of chemically ordered $(M_{2/3}^1\text{Sc}_{1/3})_2\text{GaC}$, $M^1 = \text{Cr or Mn}$, in an orthorhombic *Cmcm* structure, it should be noted that both Cr_2GaC ($\Delta H_{\text{cp}} = -19$ meV/atom) and Mn_2GaC ($\Delta H_{\text{cp}} = -31$ meV/atom) are theoretically stable, see Table SII (ref. [44]), and experimentally realized. Sc_2GaC , on the other hand, is predicted to be not stable with a formation enthalpy of $\Delta H_{\text{cp}} = +11$ meV/atom, which is reflected in lack of experimental evidence to date for that phase. For the phase stability calculations, we use the spin configuration of $(M_{2/3}^1\text{Sc}_{1/3})_2\text{GaC}$ of lowest energy, and evaluate it with respect to all other competing phases within each quaternary system, see Table SI in supplemental material (ref. [44]) for a complete list. The results for the phase stability prediction of $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ is given in Table II. Both phases are stable with a formation enthalpy ΔH_{cp} of -82 and -100 meV/atom, respectively, which compared to known ternary MAX phases indicate highly stable compounds [46,51]. Note that for each system, the hypothetical and not yet experimentally verified phases $(\text{Sc}_{2/3}M_{1/3}^2)_2\text{GaC}$, $M^2 = \text{Cr or Mn}$, belong to the equilibrium

simplex, and when excluded from the analysis, ΔH_{cp} decreases to -83 and -114 meV/atom, i.e., giving an even further increased stability.

Table II. Calculated formation enthalpy ΔH_{cp} and equilibrium simplex $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$.

Phase	equilibrium simplex (most competing phases)	ΔH_{cp} (meV/atom)	Notes
$(Cr_{2/3}Sc_{1/3})_2GaC$	Cr_3C_2 , $ScGa_2$, $(Sc_{2/3}Cr_{1/3})_2GaC$	-83	all competing phase included
$(Mn_{2/3}Sc_{1/3})_2GaC$	Mn_2GaC , $(Sc_{2/3}Mn_{1/3})_2GaC$	-100	all competing phase included
$(Cr_{2/3}Sc_{1/3})_2GaC$	$ScGa_2$, Cr_3C_2 , $ScCrC_2$, Cr_7C_3	-84	excluding $(Sc_{2/3}Cr_{1/3})_2GaC$ as competing phase
$(Mn_{2/3}Sc_{1/3})_2GaC$	$ScGa_2$, C , $Mn_{23}C_6$, Sc_3C_4	-114	excluding $(Sc_{2/3}Mn_{1/3})_2GaC$ as competing phase

B. Materials synthesis and analysis

The XRD patterns of $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$ are shown in Fig. 2 (a) and (c), with corresponding simulated pattern from the relaxed cell in (b) and (d). Peaks originating from the *i*-MAX phases are marked with an asterisk. The 110 peak, which is typically found in *i*-MAX phases due to the in-plane chemical order in the *M* plane, is seen in both samples at a 2θ angle of 19.55° and 19.60° for $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$ respectively. The Cr_2GaC or Mn_2GaC MAX phases were not observed in respective samples, as their slightly different lattice parameters compared to the *i*-MAX would give rise to peaks shifted about 0.2° towards higher 2θ angles. Similar to both Cr_2GaC and Mn_2GaC , the intensity of the 002 peak is very low, barely visible in the diffractograms. The peaks not marked in the diffractograms correspond to phase impurities, identified as C (graphite), Cr_2GaC , Sc_2O_3 , and $CrGa_4$ for the $(Cr_{2/3}Sc_{1/3})_2GaC$ sample and C, Sc_2OC , Mn_3GaC , and Ga_3Sc for the $(Mn_{2/3}Sc_{1/3})_2GaC$ sample.

The lattice parameters for the *i*-MAX phases obtained from X-ray diffraction are $a=9.071 \text{ \AA}$, $b=5.207 \text{ \AA}$, and $c=12.772 \text{ \AA}$ for $(Cr_{2/3}Sc_{1/3})_2GaC$ and $a=9.004 \text{ \AA}$, $b=5.187 \text{ \AA}$, and $c=12.630 \text{ \AA}$ for $(Mn_{2/3}Sc_{1/3})_2GaC$. This is in line with the trend for Mn_2GaC [18] as compared to Cr_2GaC [15], with smaller lattice parameters for the former phase.

Figure 2. Measured XRD patterns of (a) $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and (c) $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$, and calculated diffraction pattern of (b) $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and (d) $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$.

Figure 3. HRSTEM images of $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ viewed along zone axes (a) $[100]$ and (b) $[110]$, and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ viewed along zone axes (c) $[100]$ and (d) $[110]$. Schematic representations are based on the atomic arrangement in an orthorhombic structure of space group $Cmcm$, and are shown overlaid on the STEM images.

Figure 3(a) and 3(b) show the high-resolution STEM (HRSTEM) images of $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ viewed along zone axes $[100]$ and $[110]$, respectively, together with corresponding schematic illustrations for an orthorhombic structure of space group $Cmcm$ (#63). Figures 3(c) and 3(d) show correspondingly $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ viewed along zone axes $[100]$ and $[110]$. For the $[100]$ zone axis, the structure looks identical to that of a traditional MAX phase when viewed along $[11-20]$, with contrast contribution from both Sc and Cr/Mn atoms. For Figure 3(b) and 3(d), the $[110]$ oriented image is obtained by rotating the sample $\pm 30^\circ$ with respect to a perpendicular out-of-plane axis from the $[100]$ orientation. Although not very pronounced, there is a contrast difference when comparing Sc and Cr/Mn atoms, indicating chemical order in the M layer. The two orientations shown in Figure 3 is sufficient for concluding that both materials belong to an orthorhombic structure of space group $Cmcm$ (63). Further, local STEM-EDX analysis showed a Cr/Mn:Sc:Ga ratio of approx. 4:2:3 for the respective sample, which is consistent with the ideal i -MAX composition.

Previous reports show that bulk synthesis of a MAX phase is associated with challenges in incorporation of a large concentration of Mn [20]. In the present work, we have realized a Mn

content of 67% on the M site through synthesis of an i -MAX phase with Mn as the majority element, which is the highest Mn content attained in a bulk MAX phase to date. Furthermore, the here obtained new phases $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ are in line with the previously reported empirical “rule” for i -MAX formation, stating that in-plane chemical ordered is possible for two M elements with a difference in metallic radius of more than 0.2 Å. Using a metallic atom radius of 1.28, 1.27, and 1.62 Å for Cr, Mn, and Sc, respectively, the difference between the M elements is 0.34 and 0.35 for $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ respectively. The chemical order is also in line with the Hume-Rothery rules for solid solutions [52], which state that a solid solution of two metals can form if the difference in atomic radii between the solvent (majority) and solute (minority) elements is below 15 %, and with the minority element having the larger atomic radius. For the here presented i -MAX phases, the difference in atomic radii is 27-28%, thus no solid solution is expected, considering also the more rigid lattice carbidic bonding of this system.

C. Simulations of the magnetic ground state

Figure 4(a) shows the calculated energy difference ΔE_{NM} for different spin configurations relative to the non-magnetic (NM) state for $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ using the PBE exchange-correlation functional. As shown, most spin configurations relax to a NM state (i.e. $\Delta E_{\text{NM}}=0$), while a few are found to be magnetic, in accordance with their initially assigned configuration and with local moments around 0.7 to 0.8 μ_B per M^I atom. Note that ΔE_{NM} is comparatively small with the lowest energy spin configuration being X2 at -1.7 meV/atom for $M^I = \text{Cr}$ and AFM1 at -1.1 meV/atom for $M^I = \text{Mn}$. The small difference in ΔE_{NM} is also reflected in small differences in their corresponding crystal structure. More detailed information of structural and magnetic information is given in Table SIII and SIV[44].

In theoretical studies on magnetic MAX phases, mostly focused on Cr-based M_2AX phases [41,53-57], the need to use DFT+U methods or not has been discussed [14]. We have previously shown that a moderate value of $U_{\text{eff}} = U - J = 1$ eV could be used for Cr_2AC ($A = \text{Al}, \text{Ga}, \text{Ge}$) [57]. Based on this we have also performed calculations on $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ with $U_{\text{eff}} = 1$ eV to explore the effect more localized 3d electrons have on the crystal and magnetic structure. Figure 4(b) shows ΔE_{NM} using PBE+U. The majority of all considered spin configurations are after relaxation still spin-polarized, where the those lowest energy are AFM-ordered, X2 at -31 meV/atom for $M^I = \text{Cr}$, and AFM1 at -39 meV/atom for

$M^I = \text{Mn}$. The localization of 3d electrons thus results in larger values of ΔE_{NM} as well as increased lattice parameters and local moments, 1.3 to 1.6 μ_B per Cr and 1.9 to 2.3 μ_B per Mn. Structural and magnetic information is given in Tables SV and SIV[44].

Based on the simulations, the suggested magnetic ground state is AFM, though close to degenerate with FM ordering. This is similar to previous theoretical predictions of magnetic MAX phases [14]. Looking at reported experimental investigations on materials related to the *i*-MAX phases presented herein, different magnetic properties have been observed for Mn-containing MAX phases [18,30,43,58,59]. $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ was identified as quasi-2D laminar ferromagnet [30] and $(\text{Mo}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ was suggested to be a soft magnetic material with competing FM and AFM interactions [59]. More detailed studies on Mn_2GaC suggested a canted AFM spin configuration with long range ordering [43,60]. The condition that $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ has a reduced Mn content compared to Mn_2GaC raises the question of the influence of Sc on the magnetic properties. From *ab-initio* simulations performed herein, no significant induced moment for Sc atoms was observed in the materials for any of the magnetic configurations calculated, and therefore it is very likely that the magnetic moment will entirely originate from Mn atoms. However, all the aforementioned reported materials were found to be soft magnetic materials, suggesting similar characteristic for the *i*-MAX phases.

Figure 4. Calculated energy difference ΔE_{NM} relative the non-magnetic (NM) solution for considered spin configurations of $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ (grey) and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ (red) using (a) PBE and (b) PBE+U with $U_{\text{eff}} = 1$ eV. Note difference in scale between (a) and (b).

IV. CONCLUSIONS

DFT calculations theoretically predicts two new *i*-MAX phases, $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ and $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$. Various magnetic configurations have been simulated using both DFT and DFT+U, and an AFM ground state has been proposed, even though being close to degenerate in energy with a FM spin configuration. Material synthesis through sintering methods confirms the existence of the predicted materials, crystallizing in an orthorhombic structure (*Cmcm*), as opposed to the majority of previously reported *i*-MAX phases which display a monoclinic structure. The present materials expand the set of *i*-MAX phases, in particular those that are presumably magnetic, further realizing a two-fold increase in the Mn content compared to previously reported MAX compositions obtained from bulk synthesis.

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References

- [1] P. Eklund, M. Beckers, U. Jansson, H. Högborg, and L. Hultman, *Thin Solid Films* **518**, 1851 (2010).
- [2] M. W. Barsoum, *Prog. Solid State Chem.* **28**, 201 (2000).
- [3] M. W. Barsoum and T. El-Raghy, *American Scientist* **89**, 334 (2001).
- [4] D. J. Tallman, B. Anasori, and M. W. Barsoum, *Mater. Res. Lett.* **1**, 115 (2013).
- [5] C. J. Gilbert, D. R. Bloyer, M. W. Barsoum, T. El-Raghy, A. P. Tomsia, and R. O. Ritchie, *Scripta Mater.* **42**, 761 (2000).

- [6] A.-S. Farle, C. Kwakernaak, S. van der Zwaag, and W. G. Sloof, *J. Eur. Ceram. Soc.* **35**, 37 (2015).
- [7] W. G. Sloof *et al.*, *Sci. Rep.* **6**, 23040 (2016).
- [8] E. N. Hoffman, D. W. Vinson, R. L. Sindelar, D. J. Tallman, G. Kohse, and M. W. Barsoum, *Nucl. Eng. Des.* **244**, 17 (2012).
- [9] D. J. Tallman, E. N. Hoffman, E. a. N. Caspi, B. L. Garcia-Diaz, G. Kohse, R. L. Sindelar, and M. W. Barsoum, *Acta Mater.* **85**, 132 (2015).
- [10] A. S. Ingason *et al.*, *Phys. Rev. Lett.* **110**, 195502 (2013).
- [11] A. Mockute, M. Dahlqvist, J. Emmerlich, L. Hultman, J. M. Schneider, P. O. Å. Persson, and J. Rosen, *Phys. Rev. B* **87**, 094113 (2013).
- [12] S. Lin, P. Tong, B. S. Wang, Y. N. Huang, W. J. Lu, D. F. Shao, B. C. Zhao, W. H. Song, and Y. P. Sun, *J. Appl. Phys.* **113**, 053502 (2013).
- [13] R. Meshkian, A. S. Ingason, U. B. Arnalds, F. Magnus, J. Lu, and J. Rosen, *APL Mater.* **3**, 076102 (2015).
- [14] A. S. Ingason, M. Dahlqvist, and J. Rosen, *J. Phys.-Condens. Mat.* **28**, 433003 (2016).
- [15] A. Petruhins *et al.*, *Phys. Status Solidi RRL* **7**, 971 (2013).
- [16] R. Meshkian, A. S. Ingason, M. Dahlqvist, A. Petruhins, U. B. Arnalds, F. Magnus, J. Lu, and J. Rosen, *Phys. Status Solidi RRL* **9**, 197 (2015).
- [17] C. C. Lai *et al.*, *Acta Mater.* **99**, 157 (2015).
- [18] A. S. Ingason *et al.*, *Mater. Res. Lett.* **2**, 89 (2013).
- [19] A. Petruhins, A. S. Ingason, J. Lu, F. Magnus, S. Olafsson, and J. Rosen, *J. Mater. Sci.* **50**, 4495 (2015).
- [20] A. Mockute, J. Lu, E. J. Moon, M. Yan, B. Anasori, S. J. May, M. W. Barsoum, and J. Rosen, *Mater. Res. Lett.* **3**, 16 (2014).
- [21] Z. Liu *et al.*, *Acta Mater.* **73**, 186 (2014).
- [22] M. Dahlqvist, J. Lu, R. Meshkian, Q. Tao, L. Hultman, and J. Rosen, *Sci. Adv.* **3**, e1700642 (2017).
- [23] Q. Tao *et al.*, *Nat. Commun.* **8**, 14949 (2017).
- [24] J. Lu, A. Thore, R. Meshkian, Q. Tao, L. Hultman, and J. Rosen, *Cryst. Growth Des.* **17**, 5704 (2017).
- [25] R. Meshkian *et al.*, *Adv Mater* **30**, e1706409 (2018).
- [26] L. Chen *et al.*, *Inorganic Chemistry* **57**, 6237 (2018).
- [27] M. Dahlqvist, A. Petruhins, J. Lu, L. Hultman, and J. Rosen, *ACS Nano* **12**, 7761 (2018).
- [28] Quanzheng Tao *et al.*, Submitted (2018).
- [29] I. P. Novoselova *et al.*, *Sci. Rep.* **8**, 2637 (2018).
- [30] R. Salikhov, A. S. Semisalova, A. Petruhins, A. S. Ingason, J. Rosen, U. Wiedwald, and M. Farle, *Mater. Res. Lett.* **3**, 156 (2015).
- [31] S. Nakatsuji, N. Kiyohara, and T. Higo, *Nature* **527**, 212 (2015).
- [32] K. Essafi, O. Benton, and L. D. C. Jaubert, *Nat. Commun.* **7**, 10297 (2016).
- [33] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [34] G. Kresse and J. Furthmüller, *Comp. Mater. Sci.* **6**, 15 (1996).
- [35] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [36] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [37] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [38] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [39] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [40] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- [41] M. Dahlqvist, B. Alling, and J. Rosen, *J. Appl. Phys.* **113**, 216103 (2013).
- [42] M. Dahlqvist, B. Alling, and J. Rosen, *J. Phys. Cond. Matter* **27**, 095601 (2015).
- [43] M. Dahlqvist *et al.*, *Phys. Rev. B* **93**, 014410 (2016).

- [44] See Supplemental Material at [url] for more details on computational methods and results.
- [45] M. Dahlqvist, B. Alling, I. A. Abrikosov, and J. Rosén, Phys. Rev. B **81**, 024111 (2010).
- [46] M. Dahlqvist, B. Alling, and J. Rosén, Phys. Rev. B **81**, 220102 (2010).
- [47] A. Thore, M. Dahlqvist, B. Alling, and J. Rosén, Comput. Mater. Sci. **91**, 251 (2014).
- [48] P. Eklund, M. Dahlqvist, O. Tengstrand, L. Hultman, J. Lu, N. Nedfors, U. Jansson, and J. Rosén, Phys. Rev. Lett. **109**, 035502 (2012).
- [49] A. S. Ingason *et al.*, Mater. Res. Lett. **2**, 89 (2014).
- [50] K. Momma and F. Izumi, J. Appl. Crystallogr. **44**, 1272 (2011).
- [51] V. J. Keast, S. Harris, and D. K. Smith, Phys. Rev. B **80**, 214113 (2009).
- [52] W. Hume-Rothery and H. M. Powell, Z. Kristallogr. Cryst. Mater. **91**, 23 (1935).
- [53] Y. L. Du, Z. M. Sun, H. Hashimoto, and M. W. Barsoum, J. Appl. Phys. **109**, 063707 (2011).
- [54] M. Ramzan, S. Lebegue, and R. Ahuja, Phys. Status Solidi RRL **5**, 122 (2011).
- [55] M. Ramzan, S. Lebegue, and R. Ahuja, Solid State Commun. **152**, 1147 (2012).
- [56] M. Maurizio and M. Martin, J. Phys.-Condens. Mat. **25**, 035601 (2013).
- [57] M. Dahlqvist, B. Alling, and J. Rosen, J. Phys.-Condens. Mat. **27**, 095601 (2015).
- [58] A. Petruhins, A. Ingason, J. Lu, F. Magnus, S. Olafsson, and J. Rosen, J. Mater. Sci., **1** (2015).
- [59] R. Salikhov *et al.*, J. Appl. Phys. **121**, 163904 (2017).
- [60] A. S. Ingason, G. K. Pálsson, M. Dahlqvist, and J. Rosen, Phys. Rev. B **94**, 024416 (2016).

Supporting information for

Theoretical prediction and experimental verification of the chemically-ordered atomic-laminate *i*-MAX phases (Cr_{2/3}Sc_{1/3})₂GaC and (Mn_{2/3}Sc_{1/3})₂GaC

Andrejs Petruhins*, Martin Dahlgqvist, Jun Lu, Lars Hultman, and Johanna Rosen*

*Thin Film Physics, Department of Physics, Chemistry and Biology (IFM), Linköping University,
SE-581 83, Linköping, Sweden*

*Corresponding author. Email: andrejs.petruhins@liu.se, johanna.rosen@liu.se

This file includes:

Tables SI-SVIII

Figures S1-S4

Table SI. Prototype structure, with corresponding structural information, and calculated total energy per formula unit for considered competing phases within present paper.

Phase	Prototype	Pearson symbol	Space group	Energy (eV/fu)
Cr	W	cI2	Im-3m (229)	-9.6430
Cr	Cu	cF4	Fm-3m (225)	-9.2408
Cr	Mg	hP2	P6 ₃ /mmc (194)	-9.2298
Mn	α -Mn	cI58	I-43m (217)	-9.1582
Mn	β -Mn	cP20	P4 ₁ 32 (213)	-9.1056
Mn	AuCu	tP4	P4/mmm (123)	-9.1297
Mn	CsCl	cP2	Pm-3m (221)	-9.0107
Sc	Mg	hP2	P6 ₃ /mmc (194)	-6.3327
Sc	Np	tP4	P4/nmm (129)	-6.2230
Sc	Sc	hP6	P6122 (178)	-6.2006
α -Ga	Ga	oC8	Cmca (64)	-3.0302
Ga	Ga	oC4	Cmcm (63)	-3.0121
Ga	Ga	mC4	C2/c (15)	-3.0119
C	C (graphite)	hP4	P6 ₃ /mmc (194)	-9.2246
Cr ₂₃ C ₆	Cr ₂₃ C ₆	cF116	Fm-3m (225)	-279.3407

Cr ₃ C	Fe ₃ C	oP16	Pnma (62)	-38.4634
Cr ₇ C ₃	Cr ₇ C ₃	oP40	Pnma (62)	-96.2272
Cr ₃ C ₂	Sb ₂ S ₃	oP20	Pnma (62)	-47.9107
Mn ₂₃ C ₆	Cr ₂₃ C ₆	cF116	Fm-3m (225)	-268.6277
Mn ₃ C	Fe ₃ C	oP16	C2/c (15)	-64.7226
Mn ₅ C ₂	Mn ₅ C ₂	mS28	Pnma (62)	-92.4925
Mn ₇ C ₃	Cr ₇ C ₃	oP40	P63mc (186)	-92.4221
MnC	NiAs	hP4	P6 ₃ /mmc (194)	-18.1687
Sc ₂ C	CdI ₂	hP3	P3m1 (156)	-23.2708
Sc ₂ C	Ti ₂ C	cF48	Fd-3m (227)	-23.2657
Sc ₄ C ₃	Th ₃ P ₄	cI28	I-43d (220)	-56.4192
ScC _{0.875}	NaCl	cF8	Fm-3m (225)	-14.9227
ScC	NaCl	cF8	Fm-3m (225)	-15.8395
Sc ₃ C ₄	Sc ₃ C ₄	tP70	P4/mnc (128)	-58.7638
Cr ₃ Ga	Cr ₃ Si (β-W)	cP8	Pm-3n (223)	-32.1352
CrGa	MnGa	hR78	R-3m (166)	-12.7091
Cr ₃ Ga ₄	Fe ₃ Ga ₄	mS42	C12/m1 (12)	-41.2187
CrGa ₄	Hg ₄ Pt	cI10	Im-3m (229)	-22.5270
Mn ₃ Ga	TiAl ₃	tI8	I4/mmm (139)	-30.9155
Mn ₃ Ga	Ni ₃ Sn	hP8	P6 ₃ /mmc (194)	-30.6467
MnGa	AuCu	tP2	P4/mmm (123)	-12.4531
MnGa	CuPt	hR32	R-3m (166)	-12.1692
MnGa	Mg	hP2	P6 ₃ /mmc (194)	-12.2589
MnGa	MnGa	hR78	R-3m (166)	-12.4090
Mn ₅ Ga ₈	Cr ₅ Al ₈	hR26	R3m (160)	-70.6863
Mn ₂ Ga ₅	Mn ₂ Hg ₅	tP14	P4/mbm (127)	-34.3720
MnGa ₄	PtHg ₄	cI10	Im-3m (229)	-22.1774
MnGa ₆	MnAl ₆	oC28	Cmcm (63)	-27.5430
Sc ₅ Ga ₃	Y ₅ Ga ₃	mS32	C12/m1 (12)	-44.9893
Sc ₁₁ Ga ₁₀	Ho ₁₁ Ge ₁₀	tI84	I4/mmm (139)	-112.2262
ScGa	TiI	oS8	Cmcm (63)	-9.0837
ScGa ₂	KHg ₂	oI12	Imma (74)	-14.0796
ScGa ₃	AuCu ₃	cP4	Pm-3m (221)	-17.3922
Cr ₃ GaC	CaTiO ₃	cP5	Pm-3m (221)	-41.0458
Cr ₃ GaC	Re ₃ B	oP20	Cmcm (63)	-41.4353
Cr ₂ GaC	Cr ₂ AlC	hP8	P6 ₃ /mmc (194)	-32.0973
Cr ₃ GaC ₂	Ti ₃ SiC ₂	hP12	P6 ₃ /mmc (194)	-50.6991
Cr ₄ GaC ₃	Ti ₄ AlN ₃	hP12	P6 ₃ /mmc (194)	-69.3788
Mn ₃ GaC	CaTiO ₃	cP5	Pm-3m (221)	-40.2921
Mn ₃ GaC	Re ₃ B	oP20	Cmcm (63)	-40.3287
Mn ₃ GaC	Cr ₃ AsN	tI20	I4/mcm (140)	-40.2893
Mn ₂ GaC	Cr ₂ AlC	hP8	P6 ₃ /mmc (194)	-31.1598
Mn ₃ GaC ₂	Ti ₃ SiC ₂	hP12	P6 ₃ /mmc (194)	-49.2157
Mn ₄ GaC ₃	Ti ₄ AlN ₃	hP12	P6 ₃ /mmc (194)	-67.0531
Sc ₃ GaC	CaTiO ₃	cP5	Pm-3m (221)	-34.2348
Sc ₂ GaC	Cr ₂ AlC	hP8	P6 ₃ /mmc (194)	-27.0471
Sc ₃ GaC ₂	Ti ₃ SiC ₂	hP12	P6 ₃ /mmc (194)	-43.0551
Sc ₄ GaC ₃	Ti ₄ AlN ₃	hP16	P6 ₃ /mmc (194)	-58.9402
Sc ₂ CrC ₃	Sc ₂ CrC ₃	oP24	Pbam (55)	-52.4688
β-ScCrC ₂	ScCrC ₂	hP8	P6 ₃ /mmc (194)	-35.8144
Cr ₂ ScGaC ₂	Cr ₂ TiAlC ₂	hP12	P6 ₃ /mmc (194)	-48.4666
Sc ₂ CrGaC ₂	Cr ₂ TiAlC ₂	hP12	P6 ₃ /mmc (194)	-45.8395
CrSc ₂ C	CuHg ₂ Ti	cF16	F-43m (216)	-27.7394

CrSc ₂ C	AlCu ₂ Mn	cF16	Fm-3m (225)	-28.4508
ScMn ₂	MgZn ₂	hP12	P6 ₃ /mmc (194)	-25.0744
MnSc ₂ C	CuHg ₂ Ti	cF16	F-43m (216)	-28.1878
MnSc ₂ C	AlCu ₂ Mn	cF16	Fm-3m (225)	-28.9198
Sc ₃ Mn ₂ Ga ₆	Sc ₃ Mn ₂ Ga ₆	oP44	Pnma (62)	-60.5657

Figure S1. Schematic representation of 12 collinear spin configurations considered for $(M_{2/3}Sc_{1/3})_2GaC$, $M^I = Cr$ or Mn , where the spin direction at each M^I site is represented by a black arrow.

Table SII. Identified equilibrium simplex and corresponding formation enthalpy for Cr_2GaC , Mn_2GaC and Sc_2GaC phases ($P6_3/mmc$ structure), and the hypothetical i -MAX phases $(\text{Sc}_{2/3}\text{Cr}_{1/3})_2\text{GaC}$ and $(\text{Sc}_{2/3}\text{Mn}_{1/3})_2\text{GaC}$. Please note that the former i -MAX phase diverge from an i -MAX structure upon relaxation, i.e. the phase is not stable for such atom configuration. Relaxation performed using the PBE exchange-correlation functional.

Phase	equilibrium simplex	Spin configuration [†]	ΔH_{cp} (meV/atom)	experimental observation
Cr_2GaC	Cr_3C_2 , CrGa_4 , Cr_7C_3	in-AFM1	-19	yes
Mn_2GaC	Mn_3GaC , C , MnGa_4	AFM[0001] ₄ ^A	-31	yes
Sc_2GaC	Sc_3GaC , ScGa_2 , Sc_3C_4	NM	11	no
$(\text{Sc}_{2/3}\text{Cr}_{1/3})_2\text{GaC}$	$(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$, ScGa_2 , Sc_3GaC , Sc_2CrC_3	NM	-5	no
$(\text{Sc}_{2/3}\text{Mn}_{1/3})_2\text{GaC}$	$(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$, Sc_3GaC , ScGa_2 , Sc_3C_4	NM	+12	no

[†] Results attained from Ref. [10] for Cr_2GaC and Ref. [11] for Mn_2GaC .

Table SIII. Calculated energy and corresponding structural and magnetic information for $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Cr atom)
NM	63	9.0569	5.1800	12.7669		0	0.00
FM	63	9.0926	5.2088	12.7481		-0.7	0.73
AFM1					goes to the NM state		
X2	63	9.0708	5.1951	12.7722		-1.7	0.72
A2					goes to the NM state		
X4	12	5.2075	9.0888	12.7550	$\beta=90.0872^\circ$	-1.0	0.79, 0.80
A4	38	12.7541	9.0600	5.1864	mix of A2 and AFM1	-0.7	0.48, 0.61
in-AFM1					goes to the NM state		
in-AFM2					goes to the NM state		
in-AFM3					goes to the NM state		
in-AFM4					goes to the NM state		
in-AFM5					goes to the NM state		
in-AFM6	63	9.0791	5.1957	12.7547		-2.7	0.63

Table SIV. Calculated energy and corresponding structural and magnetic information for $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Mn atom)
NM	63	8.9901	5.1385	12.5482		0	0.00
FM			goes to the NM state				
AFM1	63	8.9900	5.1419	12.5850		-1.1	0.72
X2			goes to the NM state				
A2			goes to the NM state				
X4	12	5.1397	8.9914	12.5611	$\beta=90.0032^\circ$ mix of A2 and AFM1	-0.2	0.24, 0.50
A4			goes to the NM state				
in-AFM1			goes to the NM state				
in-AFM2			goes to the NM state				
in-AFM3			goes to the NM state				
in-AFM4			goes to the NM state				
in-AFM5			goes to the NM state				
in-AFM6			goes to the NM state				

Table SV. Calculated energy and corresponding structural and magnetic information for $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional with +U method, where $U_{\text{eff}} = 1$ eV.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Cr atom)
NM	63	9.0533	5.1824	12.7838		0	0.00
FM	63	9.0995	5.2364	12.8101		-24	1.29
AFM1	63	9.1256	5.2570	12.8569		-23	1.57
X2	63	9.1169	5.2460	12.8462		-31	1.56
A2	63	9.1105	5.2521	12.8189		-22	1.37
X4	12	5.2422	9.1015	12.8323	$\beta=90.0220^\circ$	-28	1.30, 1.54
A4	38	12.8135	9.1030	5.2444		-24	1.29, 1.36
in-AFM1	63	9.0833	5.1917	12.7655		-1.5	0.55
in-AFM2	63	9.0572	5.1995	12.7896		-0.6	0.54
in-AFM3			goes to the NM state				
in-AFM4	63	9.0748	5.2260	12.7770		-5.7	1.00
in-AFM5	63	9.0598	5.2282	12.8228		-29	1.06
in-AFM6	63	9.1202	5.2123	12.7778		-29	1.06

Table SVI. Calculated energy and corresponding structural and magnetic information for $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional with +U method, where $U_{\text{eff}} = 1$ eV.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Mn atom)
NM	63	8.9848	5.1348	12.5553		0	0.00
FM	63	9.1086	5.2834	12.7238		-25	2.16
AFM1	63	9.0510	5.1932	12.7282		-39	1.90
X2	63	9.0618	5.2280	12.7330		-31	2.07
A2	63	9.1072	5.2792	12.6762		-26	2.31
X4	12	5.2438	9.0707	12.6985	90.2385	-28	2.05, 2.21
A4	38	12.6983	9.1109	5.2807		-26	2.34, 2.40
in-AFM1	63	9.0407	5.1684	12.6277		-4.2	1.27
in-AFM2	63	8.9809	5.2704	12.8601		-25	2.24
in-AFM3	63	9.1208	5.1892	12.7721		-22	2.10
in-AFM4	63	8.9605	5.2779	12.8983		-2.8	2.29
in-AFM5	63	9.0087	5.2494	12.7079		-15	1.92
in-AFM6	63	9.0231	5.2354	12.6943		-16	1.84

Figure S2. Schematic representation of the Cr_2GaC MAX phase and $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ *i*-MAX phase when viewed along a) [100], b) [010] and c) [110] zone axis. The primary structural difference between the MAX phase and the *i*-MAX phase is the in-plane chemical order within the *M*-layer,

to allow formation of a honeycomb pattern where the larger elements approach the A-layer. The A-layer, in turn, change its structure into Kagomé-like ordering, altogether resulting in an orthorhombic crystal structure of space group $Cmcm$ for the herein reported phases. Based on previously reported theoretical analysis of structure, bonding, and related stability, we suggest that the formation of *i*-MAX is favored for increasing size difference between the two metals, and with decreasing size of the A-element.

Figure S3. Selected area electron diffraction (SAED) of $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ along the $[100]$ (a) and $[110]$ (b) zone axis, and of $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ along the $[100]$ (c) and $[110]$ (d) zone axis.

Figure S4. Rietveld refinement of XRD data for the $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ sample.

Figure S5. Rietveld refinement of XRD data for the $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ sample.

Table SVII. Cell parameters and atom coordinates obtained from XRD Rietveld refinement at RT. Upon attempted change in occupancy (from 1.0) as well as Cr/Mn intermixing, there was no improvement in the refinement.

Space group	<i>Cmcm</i> (#63)	<i>Cmcm</i> (#63)
System	Cr-Sc-Ga-C	Mn-Sc-Ga-C
χ^2	13.0	10.1
a (Å)	9.05649(34)	8.99827(60)
b (Å)	5.21497(20)	5.19006(36)
c (Å)	12.76932(40)	12.62758(46)
$\alpha = \beta = \gamma = 90^\circ$		
M^I	Cr, 16h	Mn, 16h
	0.8364(2)	0.8364(14)
	0.3269(17)	0.3251(30)
	0.5771(3)	0.5761(4)
Sc	8f	8f
	0.0000	0.0000
	0.1671(23)	0.1815(31)
	0.3914(5)	0.3910(5)
Ga	4c	4c
	0.0000	0.0000
	0.6799(16)	0.6762(18)
	0.2500	0.2500
	8g	8g
	0.7655(5)	0.76362(9)
	0.4071(11)	0.43975(13)
	0.2500	0.2500
C	8e	8e
	0.8410(30)	0.8590(32)
	0.0000	0.0000
	0.0000	0.0000
	4b	4b
	0.0000	0.0000
	0.5000	0.5000
	0.0000	0.0000

Table SVIII. Phase purity obtained from Rietveld refinement in wt.%

System	Composition				
Cr-Sc-Ga-C	(Cr _{2/3} Sc _{1/3}) ₂ GaC 86.8%	Cr ₂ GaC 6.1%	Sc ₂ O ₃ 4.1%	CrGa ₄ 3.0%	
Mn-Sc-Ga-C	(Mn _{2/3} Sc _{1/3}) ₂ GaC 61.4%	C (graphite) 25.1%	Sc ₂ OC 6.8%	Mn ₃ GaC 3.2%	Ga ₃ Sc 3.5%