Magnetic Origins of Epitaxial MAX phase Mn_2GaC-based thin films probed by Emission Mössbauer Spectroscopy

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Outline

- Introduction & Motivation
  - Research interests in MAX phase
  - Latest research on the magnetic MAX phase Mn_2GaC thin film
  - Why the eMS study is needed
- Preliminary results
- Experimental plan
- Conclusions & Outlook

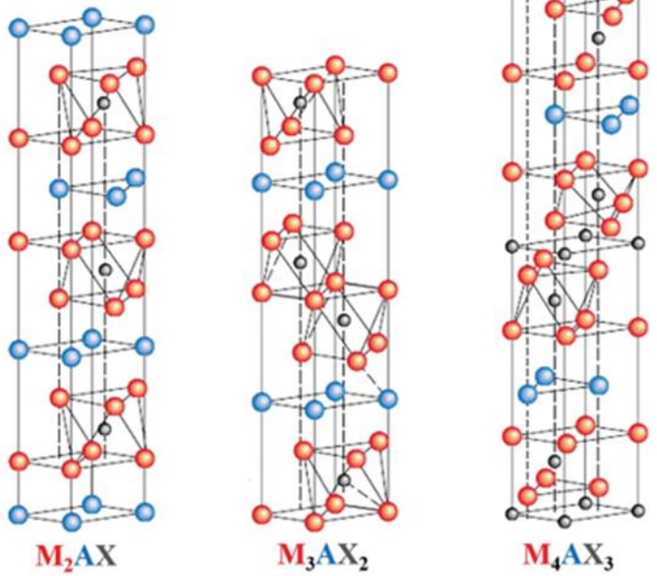
MAX phase materials

A fascinating class of inherently nanolaminated $M_{n+1}AX_n$ (n = 1, 2, 3) compounds, where M is a transition metal, A is an A-group element, and X is C and/or N.

Properties

- High electrical and thermal conductivity
- High Vickers hardness and Young's modulus
- Low frictional force
- High corrosion and oxidation resistance
- High thermal shock resistance
- High radiation damage tolerance
- Magnetism, superconductivity
- Catalyst

$M_{n+1}AX_n$ (n = 1, 2, or 3)

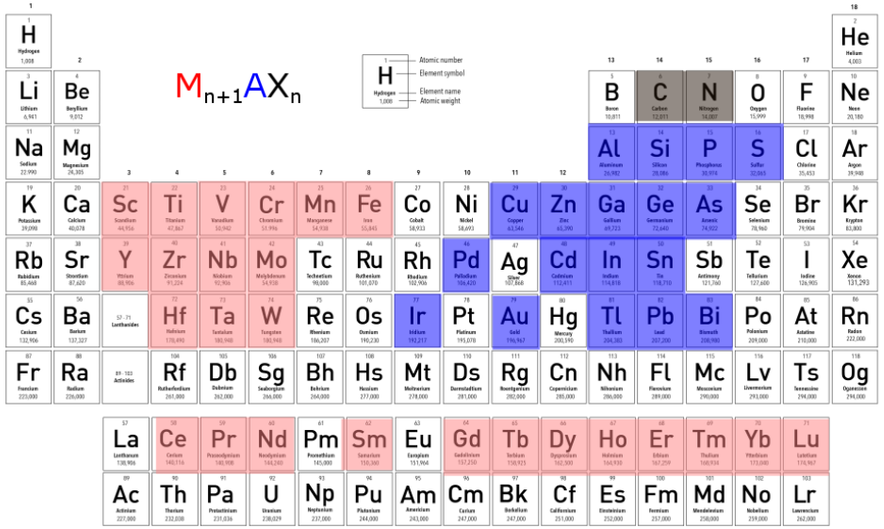


Thin films synthesis methods

Magnetron sputtering, Chemical vapor deposition, Pulsed laser deposition, Cathodic arc deposition

Applications

- High temperature electronic applications
- High temperature industrial applications
- Lubricant material
- High temperature coating material
- Microwave absorber
- Space-craft, solar panel and nuclear applications
- Spintronics
- Renewable energy



Hexagonal unit cells (P63/mmc space group) of the M_6X octahedral interleaved with single 2D layers of A element.

Strong covalent bonds along M-X-M and metallic-like bonds between M-M in basal plane; weak ionic bond between M-A along c-axis.

Unusual property combination of metals and ceramics

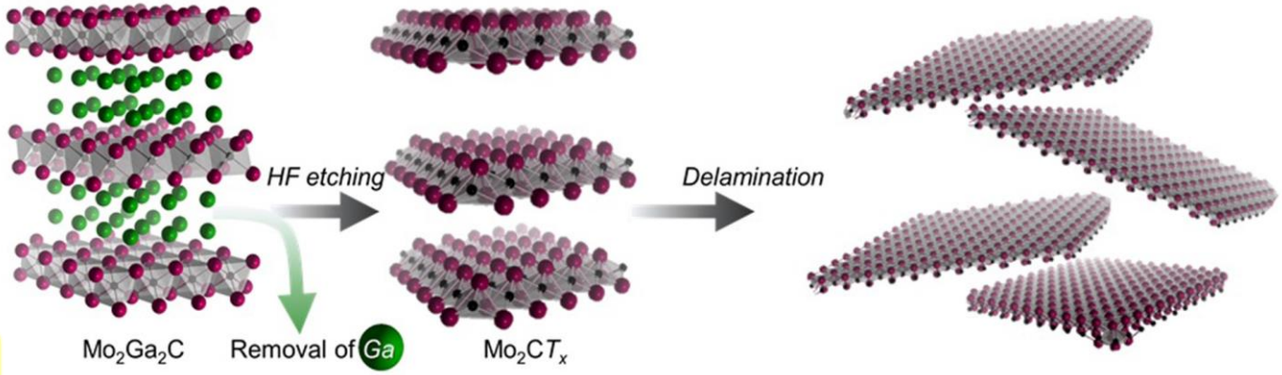
UNIVERSITY OF ICELAND

Oxf Open Mater Sci, Volume 1, Issue 1, 2021, itab020, https://doi.org/10.1093/oxfmat/itab020

From 3D to 2D: MAX to MXenes

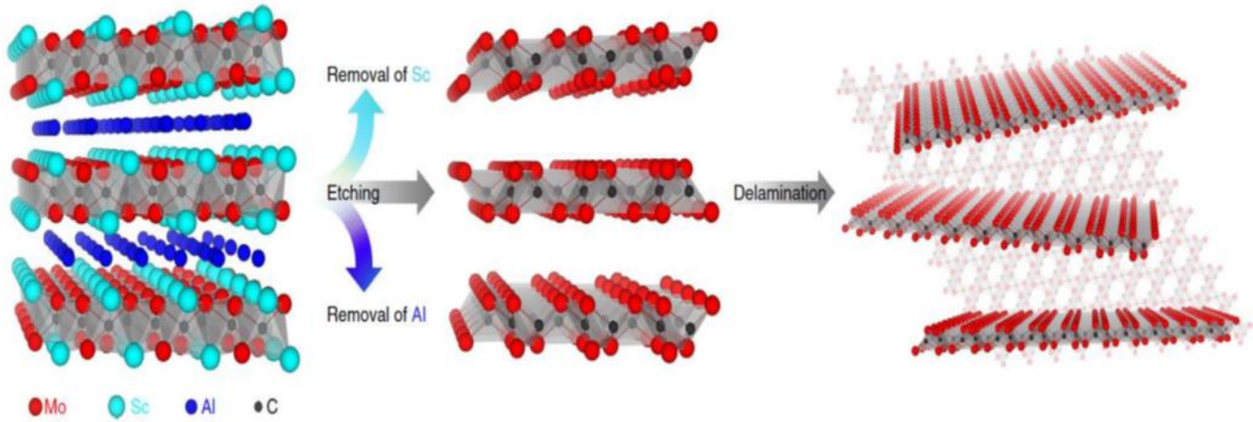
The nanolaminated nature of the MAX phases inspired an exciting path to create a graphene-like 2D transition metal carbides/nitrids $Mn_{(n+1)}X_n$, called Mxenes, by etching the weakly-bonded A elements

with remarkable composition variations and property tuning without affecting the inherent atomically laminated structure, thanks to the strongly bonded M-X-M trilayer in hexagonal structure.



Halim J et al, Adv. Funct. Mater. 26 (2016)3118

By selectively etching weakly bonded Sc and Al element in MAX phase $(Mo_{2/3}Sc_{1/3})_2AlC$, a unique 2D functional $Mo_{1.33}C$ with ordered vacancies was obtained, which shows a high electrochemical capacitance.

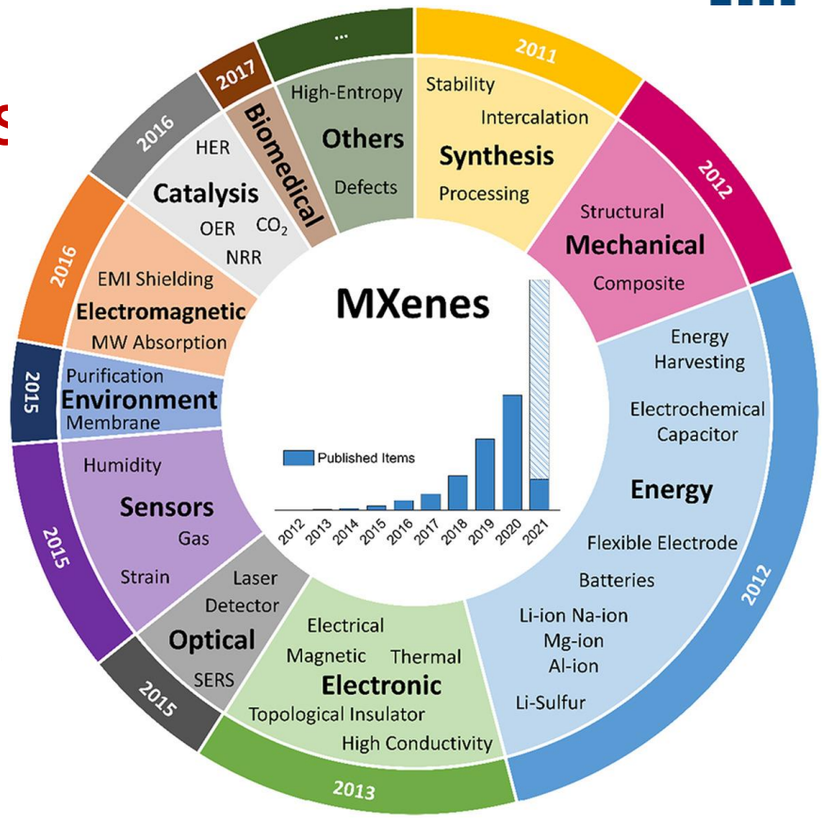


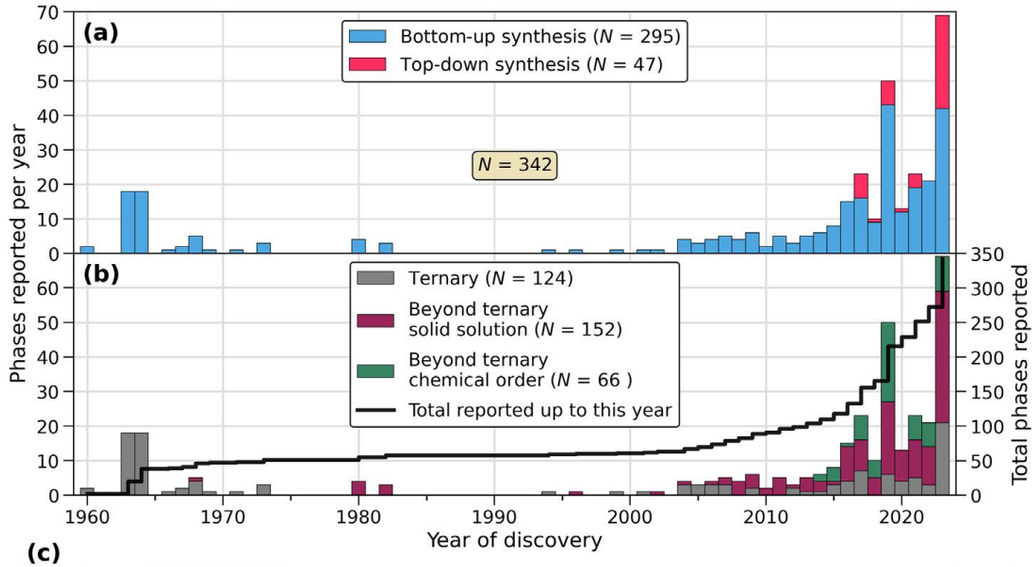
Quanzheng Tao, Linköping Studies in Science and Technology, Dissertation No. 2058

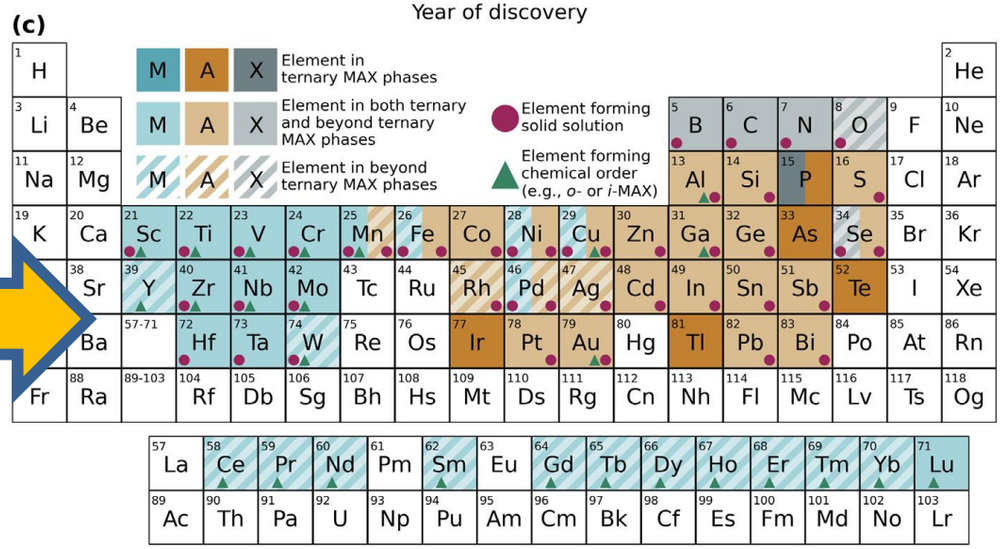
From 3D to 2D: MAX to MXenes

2D layered magnetic MXenes

- Anisotropic structure
- Fascinating magnetic characteristics e.g. spin spirals, skyrmions
- Spintronic applications.







Tremendous interests to design magnetic MAX phase with magnetic elements Mn, Cr, and Fe or alloyed with rare earth elements (RE) on the M-site or Mn, Fe, Co, and/or Ni on the A-site.

Y. Li et al.Sustainable Mater. and Tech. 34 (2022) e00516

Martin et al. Materials Today xxxx 2023; Phys. Rev. B **93**, 014410 (2016)

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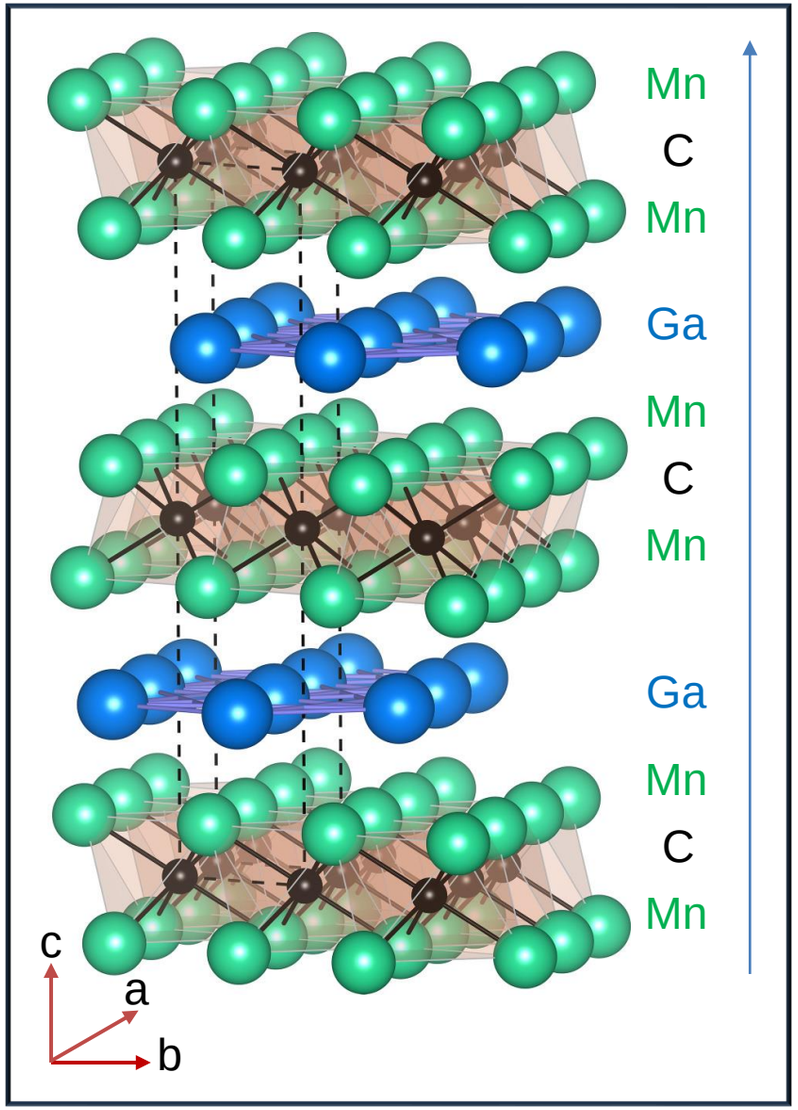
MAX phase Mn_2GaC thin film

- ❑ The first representative magnetic MAX phase with a single M-element species on the M-sites
- ❑ Epitaxial thin film grown in 2013
- ❑ Critical temperature for magnetic ordering above RT
- ❑ Additional magnetic degree of freedom to the anisotropic structural and electronic properties of the MAX phase materials

The material exhibits two magnetic phase transitions

- At ~ 507 K (T_N), the system undergoes a **magnetic order to disorder** transition from a collinear AFM state to the paramagnetic state.

- At ~ 214 K (T_t), the material undergoes a **magneto-structural phase transition** from collinear AFM at higher temperature to a non-collinear AFM spin structure, with a presence of a FM component at low temperature.



Dey et al. Phys. Rev. B 108 (2023) 054413
Ceramics International 49 (2023) 24235

Magneto-structural transformations of Mn_2GaC thin film

As a response of temperature and external magnetic field applied parallel to the film plane.

Without external magnetic field:
(I) At $T > T_t = 214$ K the system has a collinear AFM $[0001]\frac{A}{4}$ magnetic spin configuration (4 consecutive Mn-layers with the same spin direction before changing sign upon crossing a Ga layer);

The complex magnetic configuration of Mn_2GaC films is an on-going subject of research.

An external magnetic field (III) at $T > T_t$ causes the parallel spin alignment and compression of the lattice along the c-axis ($C_{III} < C_I$) delivering large negative magnetostriction of −450 ppm; (IV) at $T < T_t$ parallel spin configuration causes large positive magnetostriction of 450 ppm ($C_{IV} > C_{II}$) .

This implies that the sign of the exchange coupling between Mn moments across the Ga layers has an oscillatory-like behavior as a function of the c-axis lattice constant. These findings point to a strong coupling among magnetic, electronic and lattice structure in the layered Mn_2GaC MAX phase.

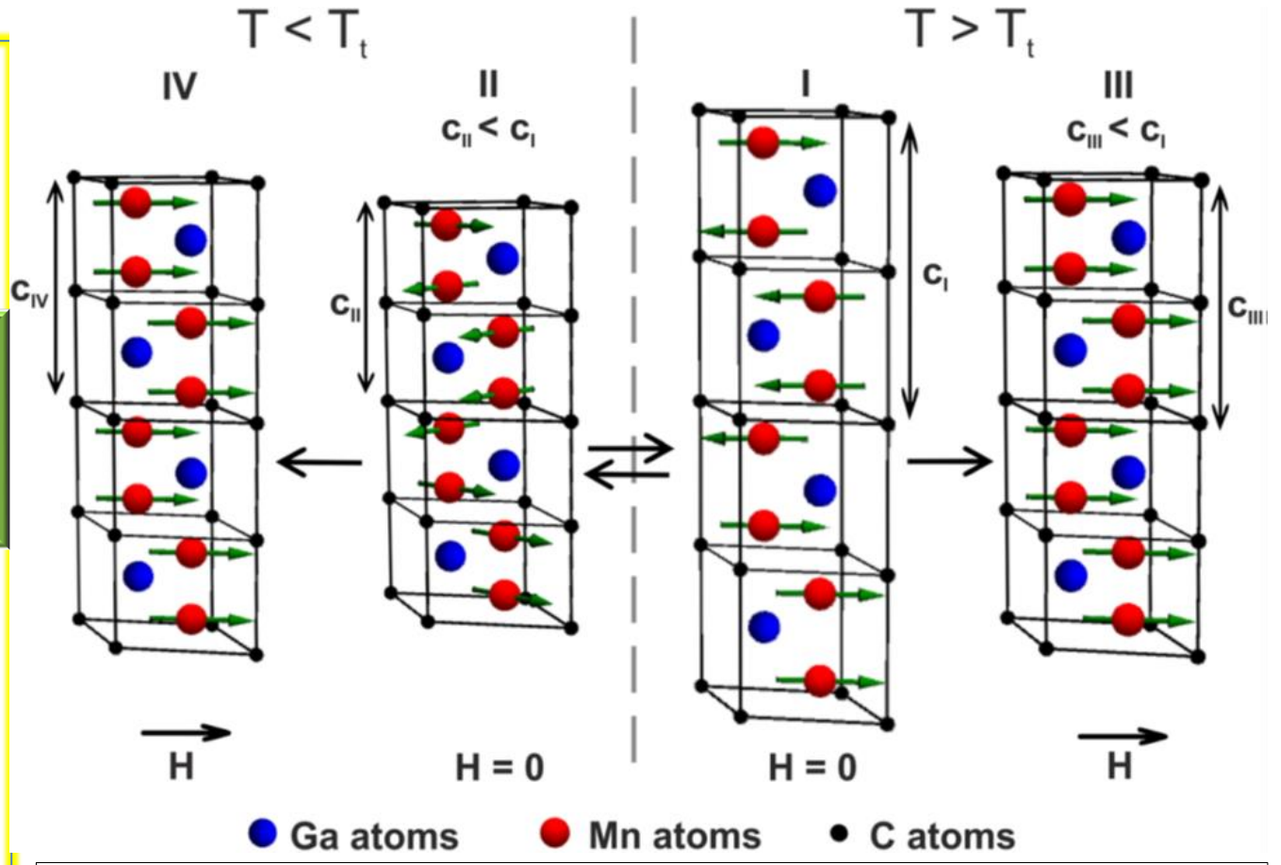


Fig.2 $T_t = 214$ K is the spin reorientation temperature, at which the magnetic structure changes from a collinear AFM state at $T > T_t$ to a non-collinear AFM configuration at $T < T_t$. This from state (I) to state (II) is accompanied by a *c*-axis lattice compression. An external magnetic field initiates a parallel spin alignment in cases (III) and (IV), causing a c-lattice compression ($C_{III} < C_I$) and expansion ($C_{IV} > C_{II}$), respectively. Novoselova et al. Sci. Rep., 8 (2018), p. 2637

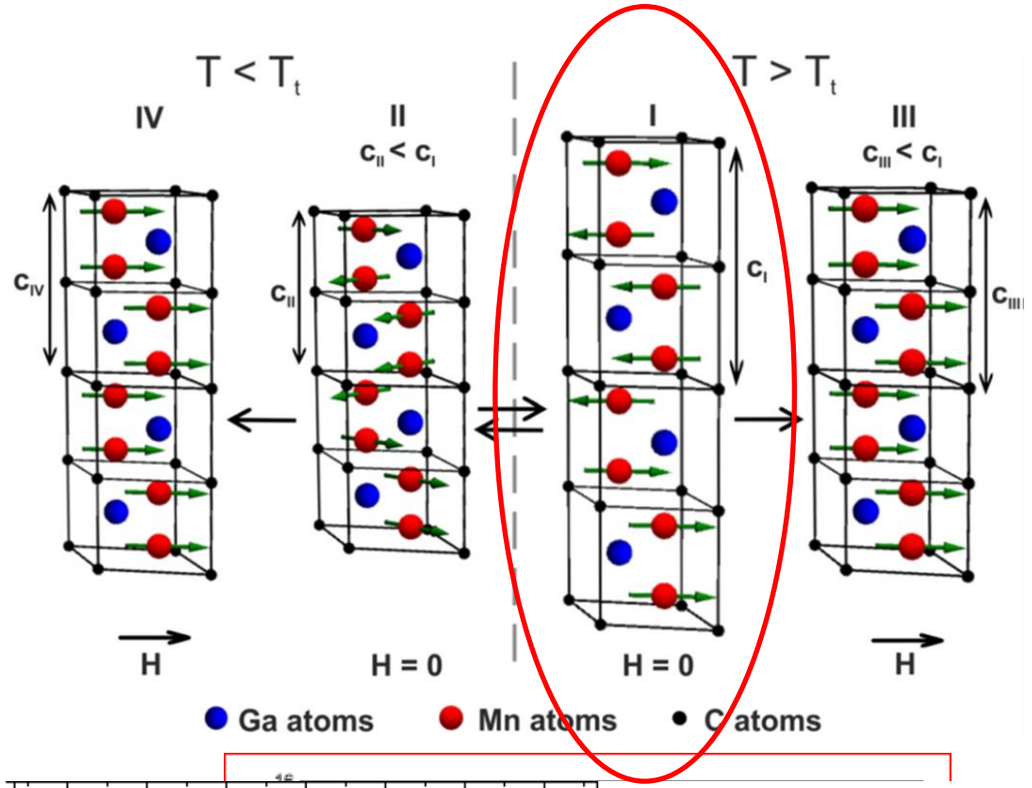
Summary of recent experimental results on the magnetic structures of MAX Mn_2GaC

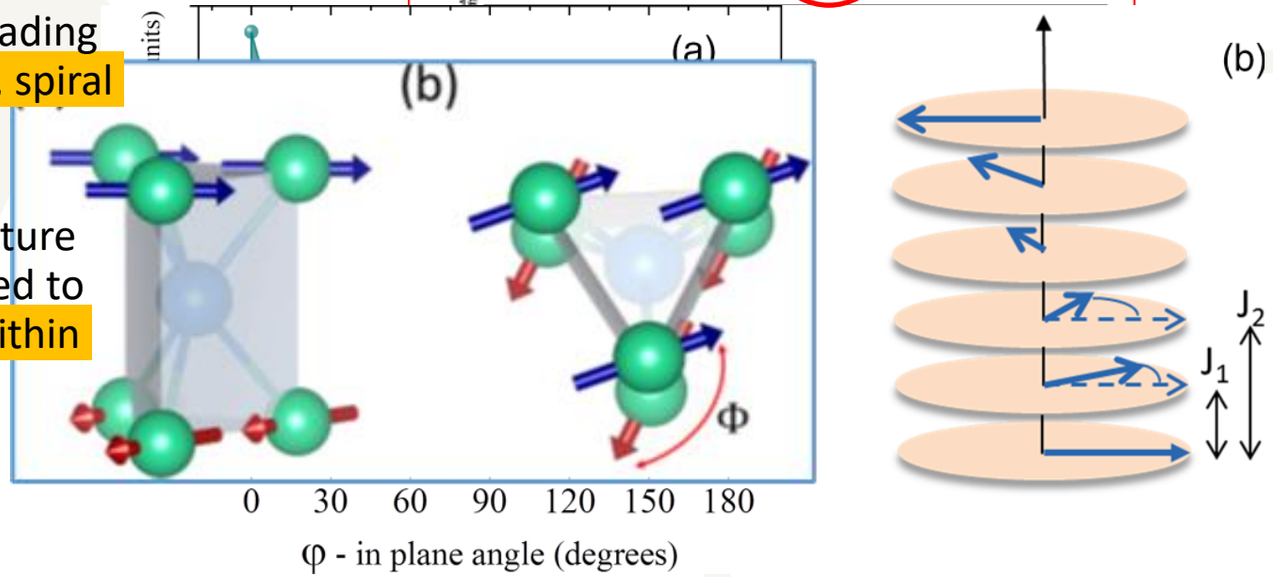
- The unpolarized neutron reflectometry (NR) suggested the theoretically predicted collinear AFM $[0001]^{\frac{A}{A}}$ magnetic spin configuration (2 consecutive FM coupled Mn-C-Mn layers before changing sign upon crossing a Ga layer), whereas a nonzero magnetic remanence suggests a long-range FM correlation.

- The preliminary zero-field NMR suggests the non-collinear arrangement of Mn moments across a Ga layer.

- The in-field NMR investigations performed indicate the presence of competing ferro- and antiferromagnetic interactions, leading to a complex, non-trivial magnetic structure (e.g. a helical, spiral magnetic structure).

- Extensive study of magnetic interactions and magnetic structure in other Mn_2GaC-based MAX phase thin films are still needed to determine the type and strength of magnetic interactions within the magnetic M layers and across the A and X layers, with various chemical compositions.

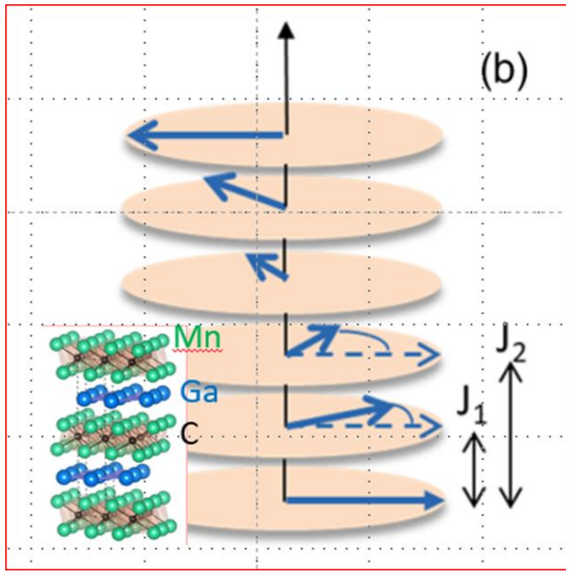


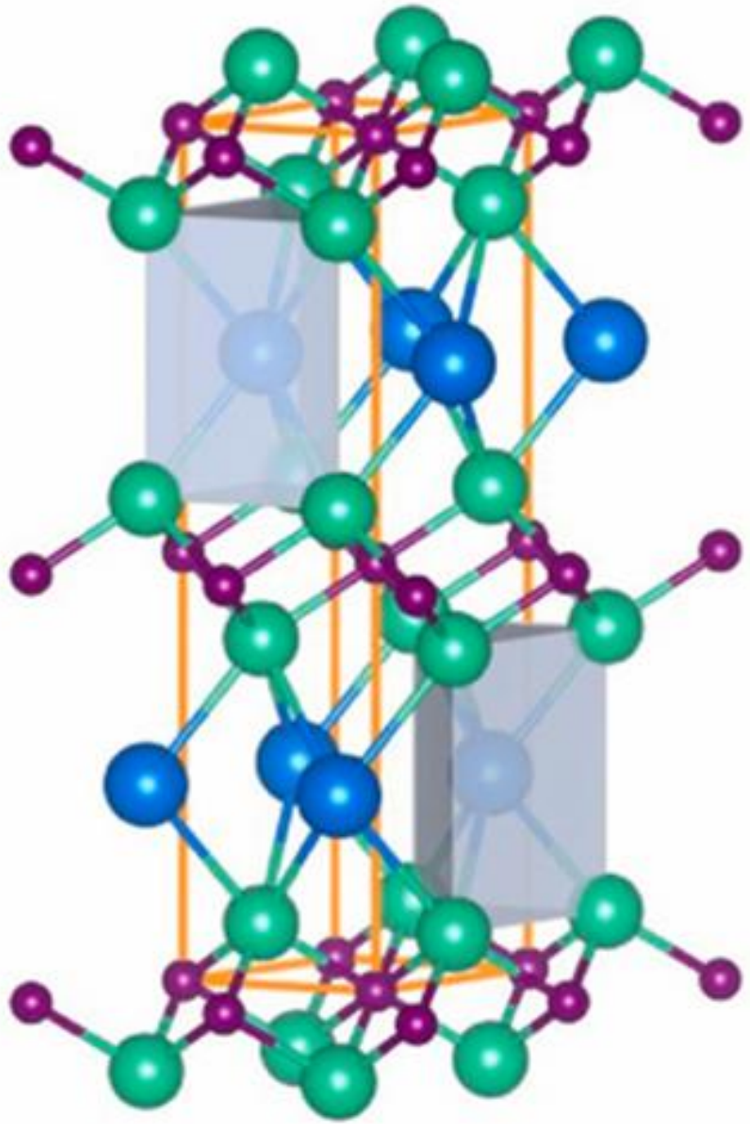


Motivation

- The findings up to date give mostly an outline or global representation of the magnetic properties of the Mn_2GaC thin films.

- Experimental studies of the local magnetic and structural interactions at substitutional atomic lattice sites with changes of temperature, magnetic field, chemical composition, chemical order, disorder in the laminated structures of the MAX phase thin films are still lacking.



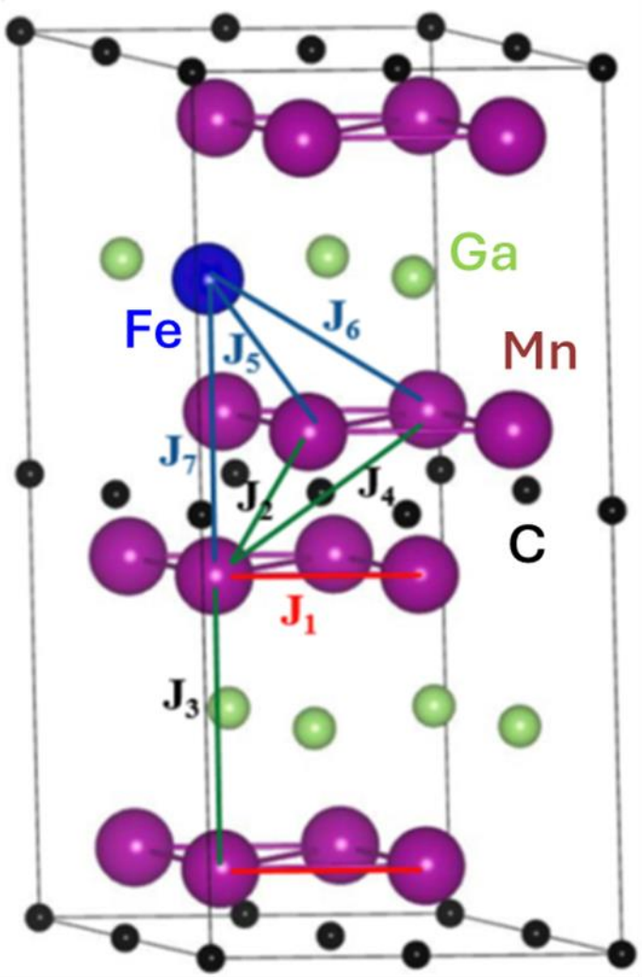


Motivation

- Aforementioned studies strongly indicate that the magnetic properties of the MAX phase material are closely associated with the in-plane local site of the M and A elements as well as the out-of-plane M-A exchange interactions in the laminated structures.

- Therefore, it is important to understand the effects of both the lattice site and the interlayer interaction of M and A elements on the magnetic properties of the MAX phase material to fine tun the magnetic properties by chemical composition, order, and crystal structure.

- These point a high necessity of applying the local probes like emission Mössbauer spectroscopy (eMS).



Draganyuk et al. *J. of Magnetism and Magnetic Materials 563 (2022) 169860*

Motivation

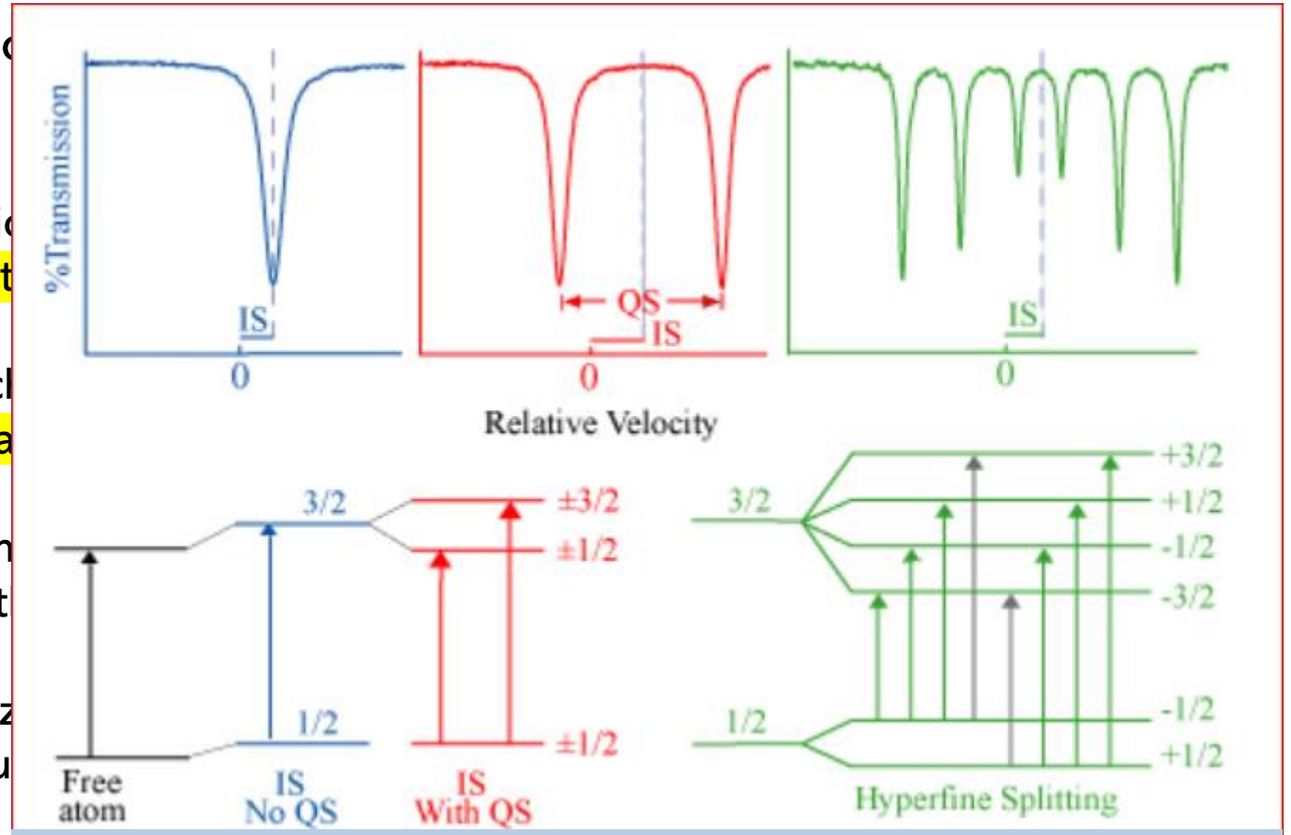
Mössbauer spectroscopy (MS) gives amc
current proposal

- The position of resonances gives informatic
can be used to determine the charge/spin st

- The relative intensity of the spectrum whicl
distinguish the probe entering the regular la

- Quadrupole splitting of spectral componen
the probe nuclei can be used to determine t

- Hyperfine Magnetic interactions characteriz
case of ^{57}Fe and ^{119}Sn can give simultaneou
site symmetry.



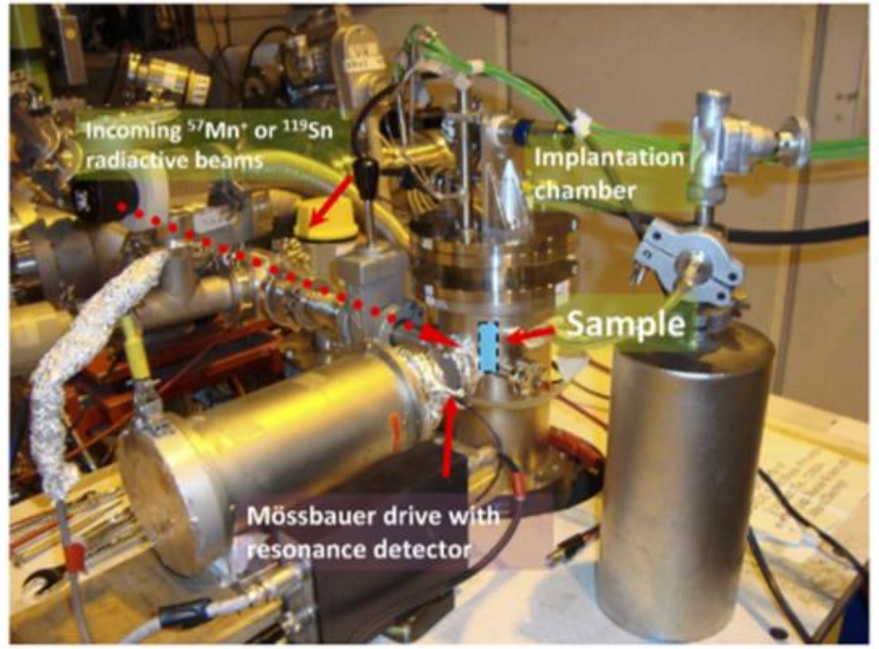
https://serc.carleton.edu/download/images/9091/dyar_MSspectra_fig3.jpg

- Temperature-dependent site populations can be used to study the nature of intrinsic or post implantation induced lattice defects in the crystal structure and co-related magnetic properties of the material.

Motivation

- The main characterization technique in this proposal is ^{57}Fe and ^{119}Sn eMS following implantation of ^{57}Mn ($T_{1/2}$= 1.45 min.) and ^{119}In ($T_{1/2}$ = 2.4 min.), respectively.

- The samples are held in a multi-purpose implantation chamber and the 14.4 keV and 23.9 keV γ-ray emission is measured with a resonance detector equipped with ^{57}Fe in a stainless steel or Ca^{119}SnO$_3$ electrode mounted on a conventional Mössbauer drive system outside the implantation chamber.



- Two main properties that eMS using ^{57}Mn and ^{119}In isotopes at ISOLDE is superior to conventional MS using doped samples: (1) The concentration required (<10^{-3} at. %) is a fraction of what is required for MS (~0.1 at. %) and (2) the timescale of the experiments is minutes with eMS compared to days with conventional MS.

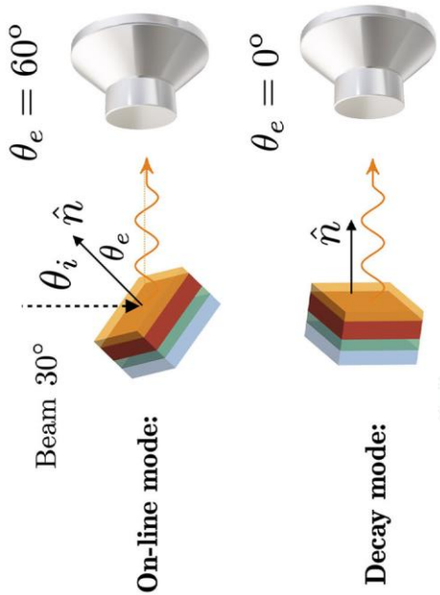
- Both these properties eliminate the possibility of precipitation and one can safely assume that the Mn/Fe and In/Sn are dilute in the samples

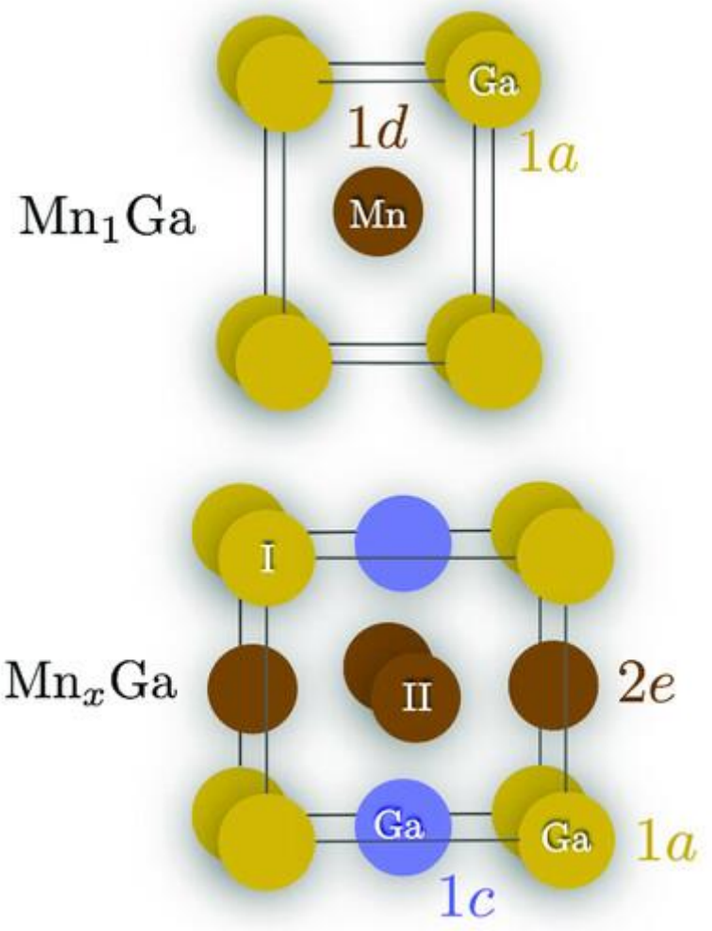
Previous eMS study using ^{57}Mn and ^{119}In isotopes at ISOLDE on MnxGa alloy

This technique has shown the success to correlate the Mn and Ga site-specific chemical, structural, and magnetic properties of binary Heusler alloy MnxGa, as a function of x, with their macroscopic magnetisms

Hyperfine magnetic fields of Mn/Fe (at Mn or Ga sites) are found to be quite sensitive to the local strain induced by the implantation.

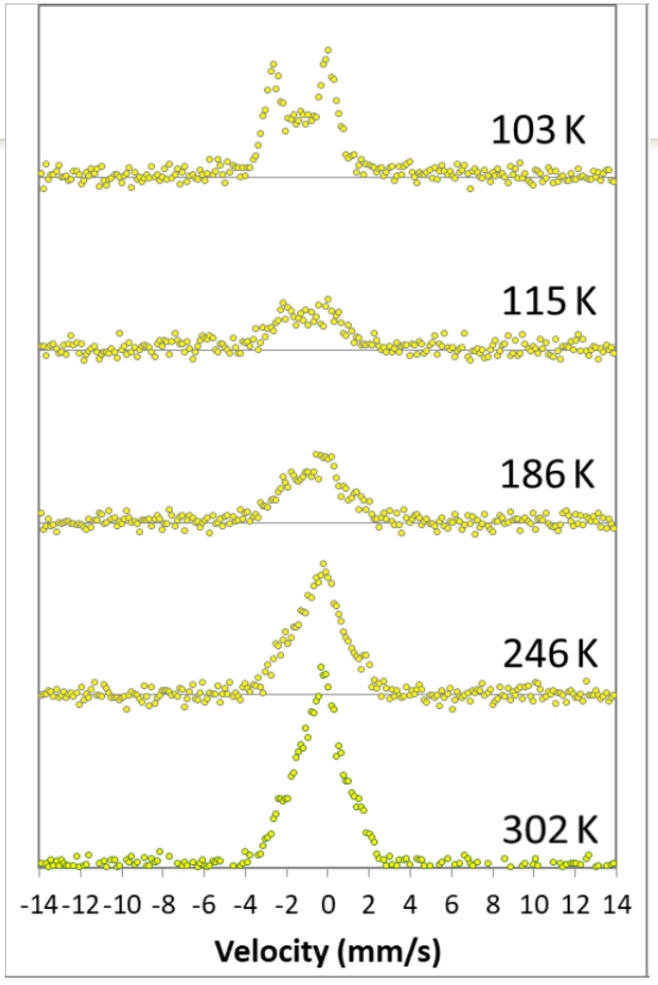
In/Sn probes are much less sensitive to the strain state as well as to the local distortions induced by the implantation damage than the ^{57}Fe probe atoms.



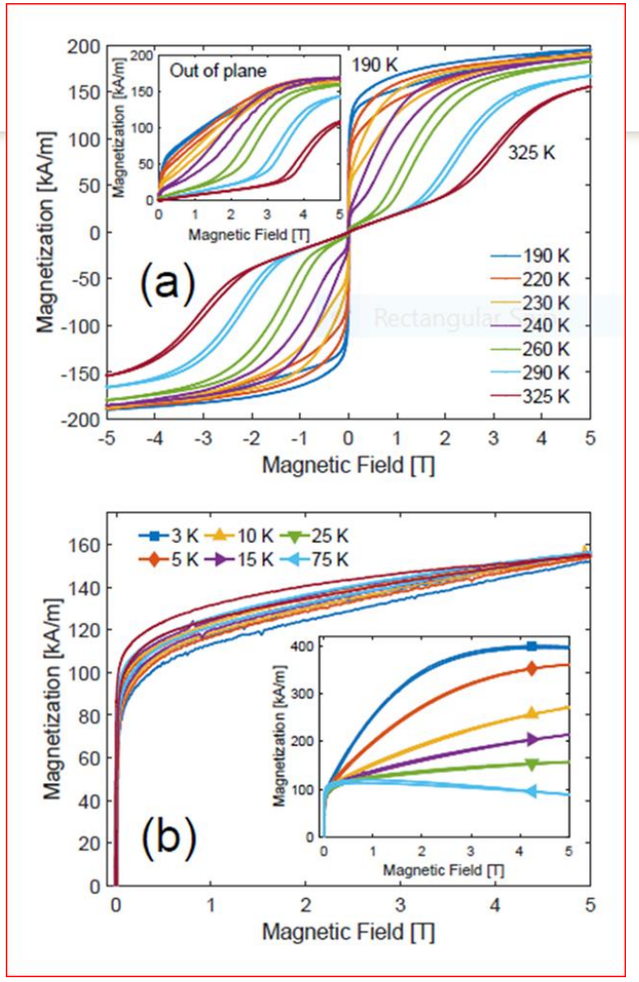


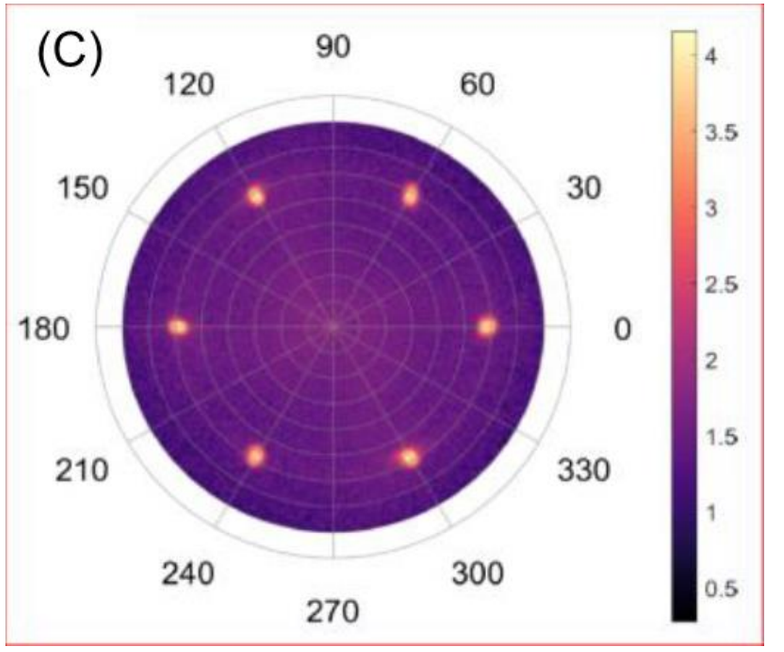
Unzueta et al. Phys. Status Solidi B 2022, 2200121

Preliminary eMS Test



- With this in mind, we tested the possibility of the ^{57}Mn eMS to study the MAX phase Mn_2GaC thin film during the Mn beamtime in 2023 at ISOLDE.





Preliminary eMS Results

From visual inspection of the spectra, we can observe that, there is a broad transition centred at ~210 K.

The spectra at 302 K and 246 K both show a broad feature centred at isomer shift δ ~ 0 - 0.3 mm/s indicating dominantly Fe^{3+} paramagnetic state and a broad feature.

It could be interpreted as magnetic feature owing to Fe with magnetic moment up to 1μB, or due to unresolved quadrupole interaction or implantation-induced internal stresses/strains which altered magnetic order as noted in Mn_xGa compounds.

These possibilities can be distinguished with further angular dependent measurements with and without external magnetic field, and post-implantation annealing measurement.

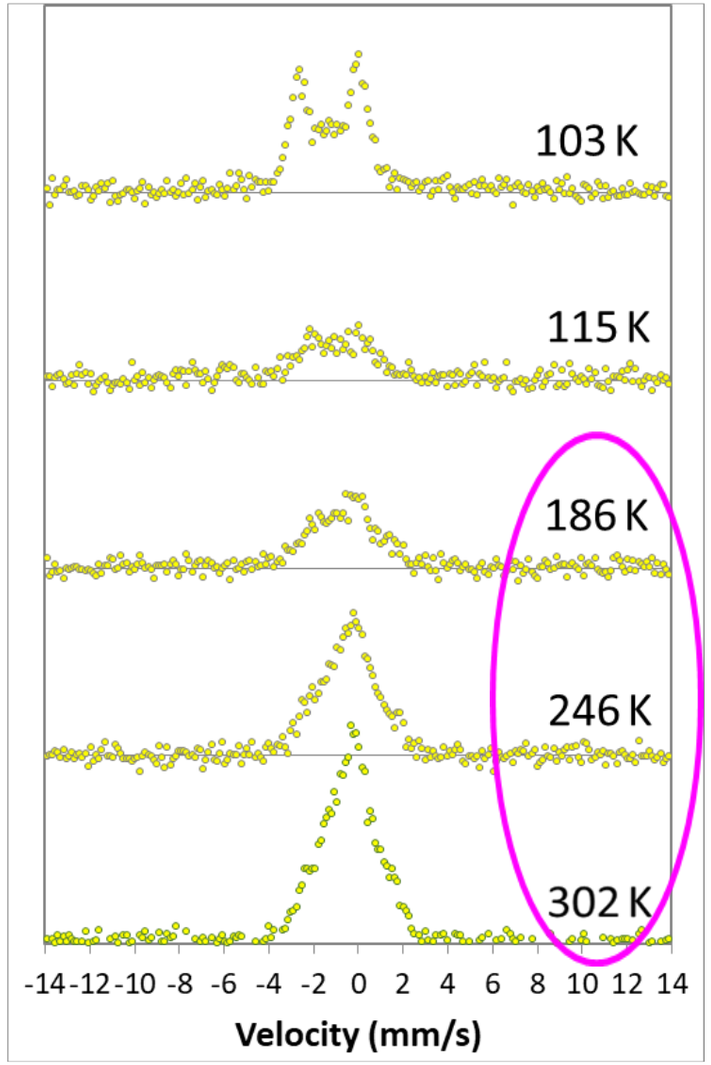


Fig.6 Preliminary eMS results of the MAX phase Mn_2GaC thin film measured from 300 K to 100 K.

Preliminary eMS Results

The spectra at 186 K and 115 K show a weakening of the central peak and an enhancement of the apparent sextet feature.

The spectral area in Mössbauer spectroscopy depends on the temperature-dependent Debye-Waller factor, which in first approximation decreases exponentially with temperature, a behaviour that is not represented in the experimental data.

Secondly, the compression of the C-lattice in the crystal structure below 210 K would expect an increased spectral area, also opposite to what is measured experimentally.

This suggests that the bond strength in the crystal structure of MAX phase Mn_2GaC needs deep understanding.

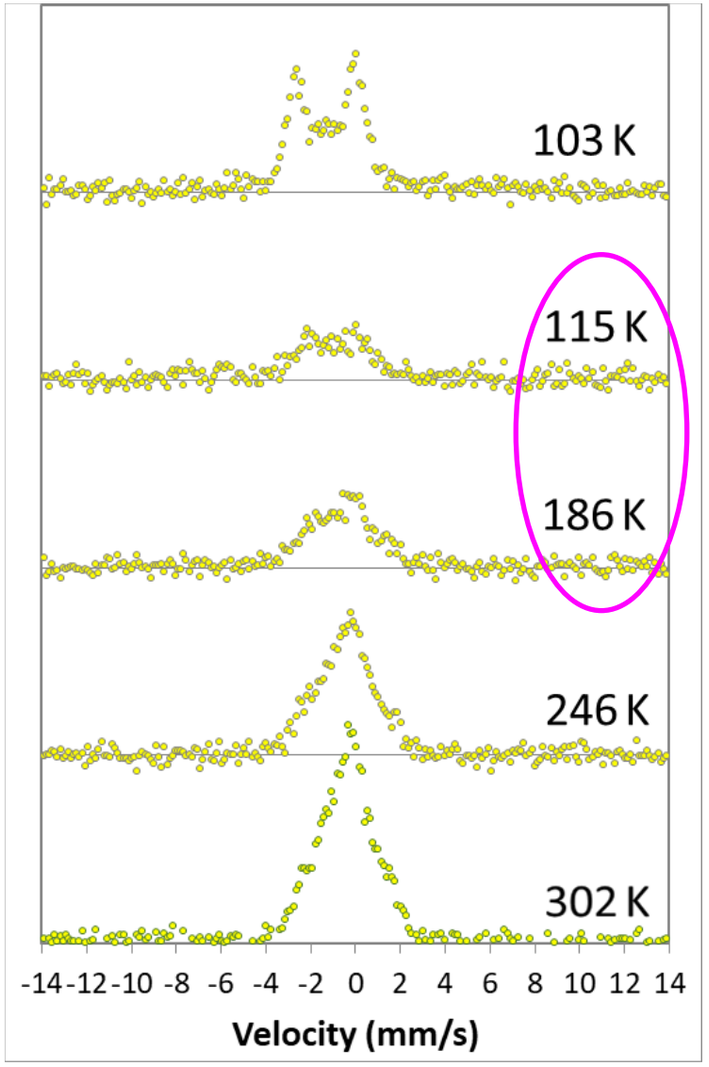


Fig.6 Preliminary eMS results of the MAX phase Mn_2GaC thin film measured from 300 K to 100 K.

Preliminary eMS Results

The sudden emergence of a new peak area below 115 K is most probably due to ice forming on the surface of the sample below 115 K due to technical reasons. This should be verified thoroughly with further eMS measurement performed at both the high and low temperatures.

As also pointed out by the eMS results obtained on the MnxGa samples, the implantation damage at low temperature can be completely annealed at 295 K and beyond, and before reaching the Curie-T, the magnetic features became more visible over the damage.

High temperature measurements are likewise very much needed to study the structure-related magnetic properties of the MAX phase material.

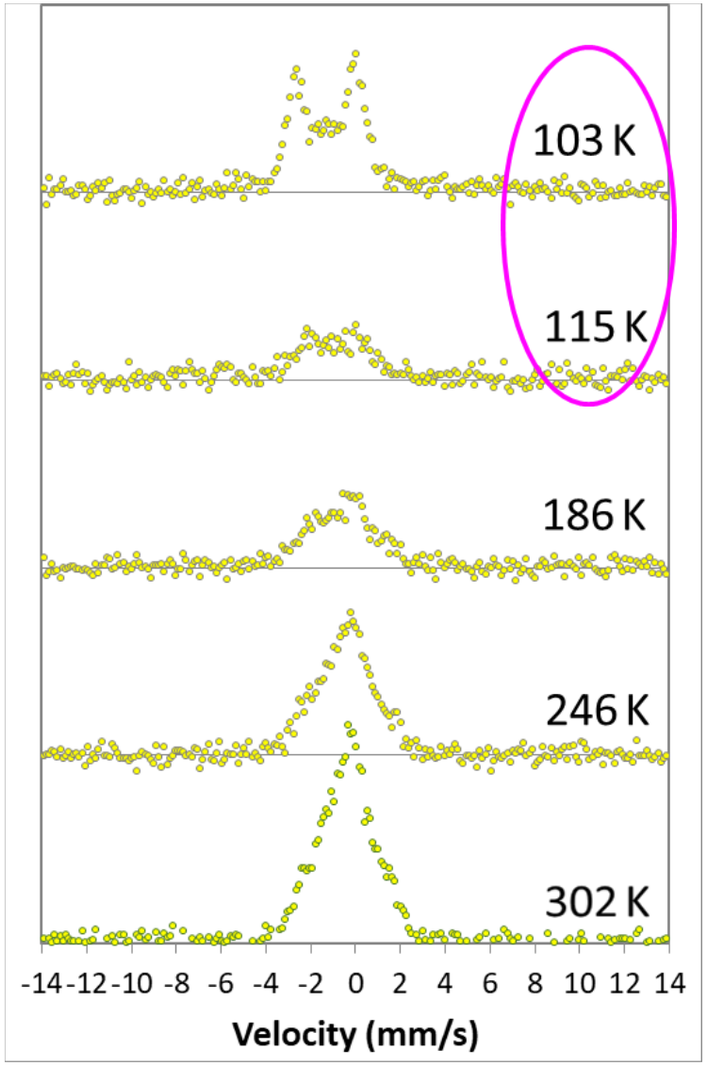
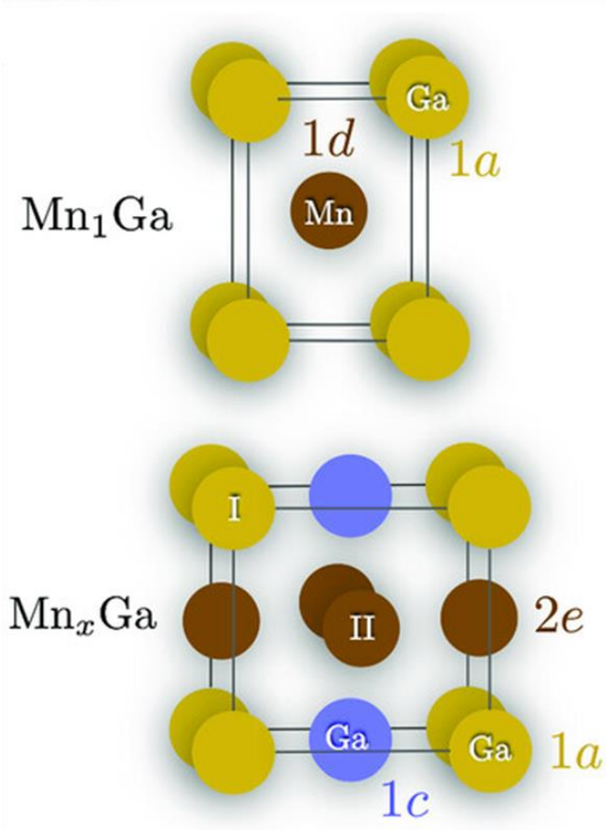


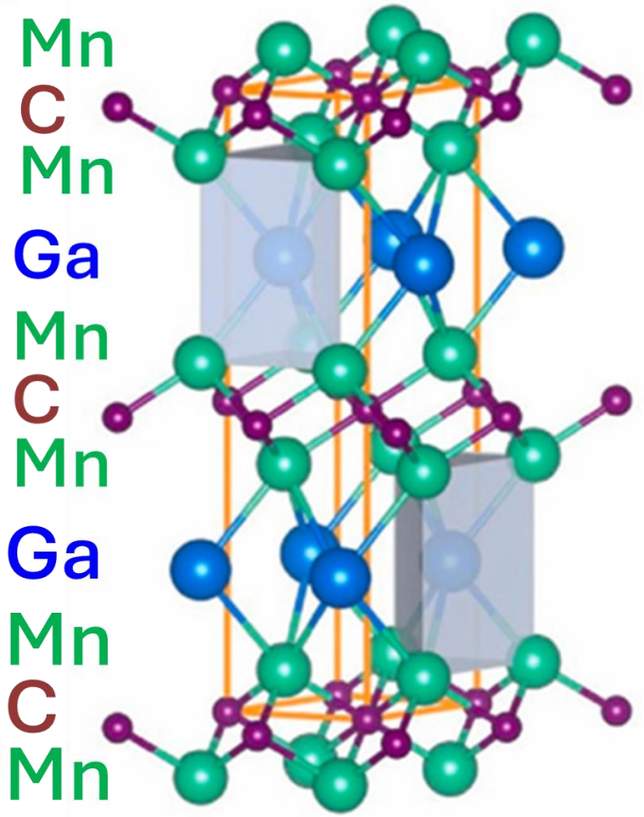
Fig.6 Preliminary eMS results of the MAX phase Mn_2GaC thin film measured from 300 K to 100 K.

Preliminary eMS Results

The crystal structure, chemical order/bond and electronic band structure of Mn and Ga atoms in MnxGa alloys and MAX phase Mn_2GaC are completely different.

To fully understand the eMS results we obtained and to gain a deep understanding about how the nanolaminated structures interrelate with the rich magnetic properties of the MAX phase Mn_2GaC, further study with both ^{57}Mn and ^{119}In eMS are highly desired.





Tetragonal $L1_0$ structure of Mn_xGa
(x = 1, top;x ≠ 1, bottom)

Hexagonal layered structure of MAX phase Mn_2GaC film: Mn atoms strongly bonded with C atoms forming Mn_6C octahedral structure in Mn-C-Mn tri-layers; the six nearest Mn neighbors around a Ga atom forming a trigonal prism along Mn-Ga-Mn interlayer

Samples and pre-characterization

Based on the stability predictions by DFT theory at Linköping University, a series of high-quality epitaxial MAX phase $(Mn_{1-x}Cr_x)_2GaC$ (x = 0.00-0.29) thin films (140-220 nm) were synthesized by direct current (DC) magnetron sputtering on 1 × 1 cm2 MgO (111) substrates at University of Iceland.

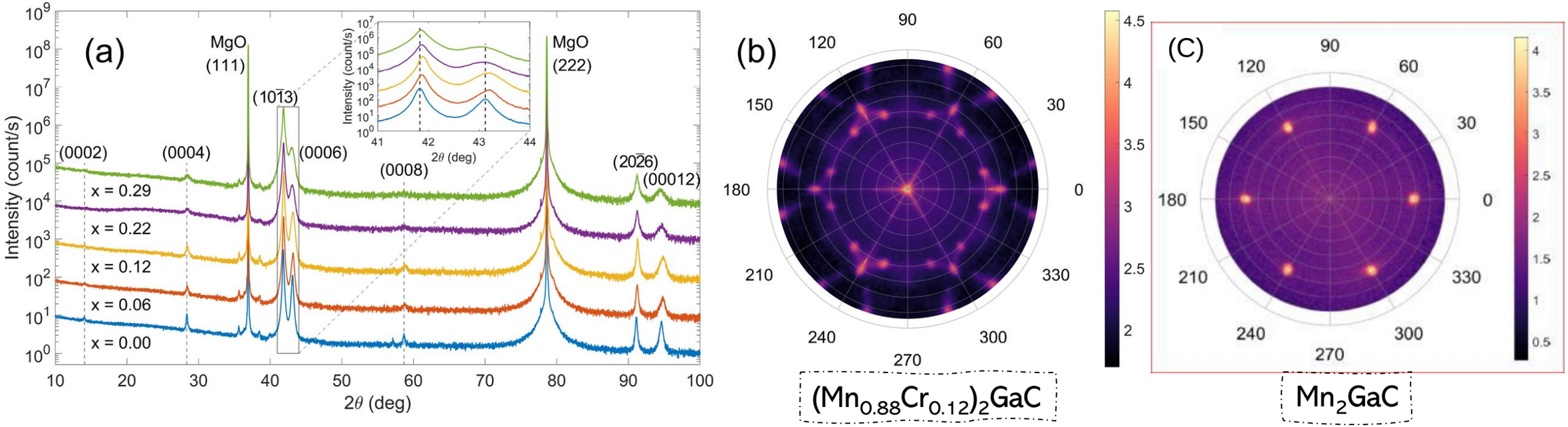


Fig.7 Phase analysis and crystal structure. (a) XRD overview scans of $(Mn_{1-x}Cr_x)_2GaC$ with *x* in the range 0.00-0.29. All samples show distinctive MAX phase peaks. The inset is an enlargement of the region containing the main film peaks of (1013) and (0006), showing that the films have two distinct growth orientations. The (1013) plane has a tilt of 59° with respect to the (0006) plane; (b, c) Pole figures for the (1013) peak at 2θ = 41.84° of the 51% (1013) and 49% (0006) oriented $(Mn_{0.88}Cr_{0.12})_2GaC$ film, and single (0006) orientated Mn_2GaC film respectively, the discrete sixfold symmetric points demonstrate the epitaxial relationship between the film and the substrate and is representative of the sample series.

Thorsteinsson et al. Phys. Rev. Mater. 7, 034409 (2023); APL Mater. **11**, 121102 (2023)

Magnetization measurements of Mn_2GaC thin film

- In-plane measurement at temperatures above the magnetic phase transition, with the inset showing out-of-plane measurements
- Below ~210 K the film exhibits ferromagnetic-like (FM-like) behavior with a remanent magnetization of 0.18 μB/Mn atom.
- At ~210 K, a magnetic phase transition occurs to an AFM state, but a metamagnetic (non-collinear/canted AFM) transition is observed at increasingly high fields with increasing temperature.
- Mn_2GaC has a magnetocrystalline anisotropy with (0 0 0 l) as easy planes.
- At low temperature range of 75 K-3 K, the high-field magnetization at 5 T remains almost constant at a value of 155 kA/m or 0.38 *μB*/Mn atom, indicating if there exists low temperature canted AFM spin state, the canting angle is constant with temperature.

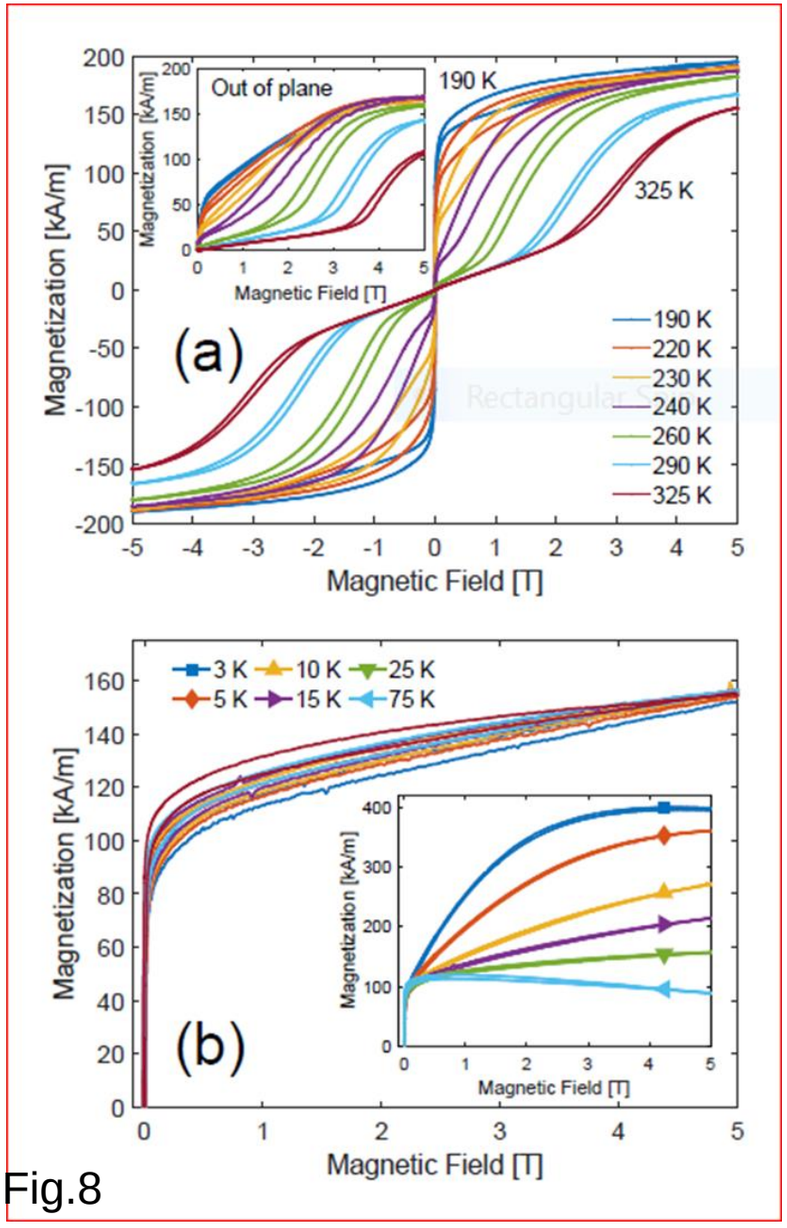


Fig.8

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Magnetization measurements of $(Mn_{1-x}Cr_x)_2GaC$ thin film

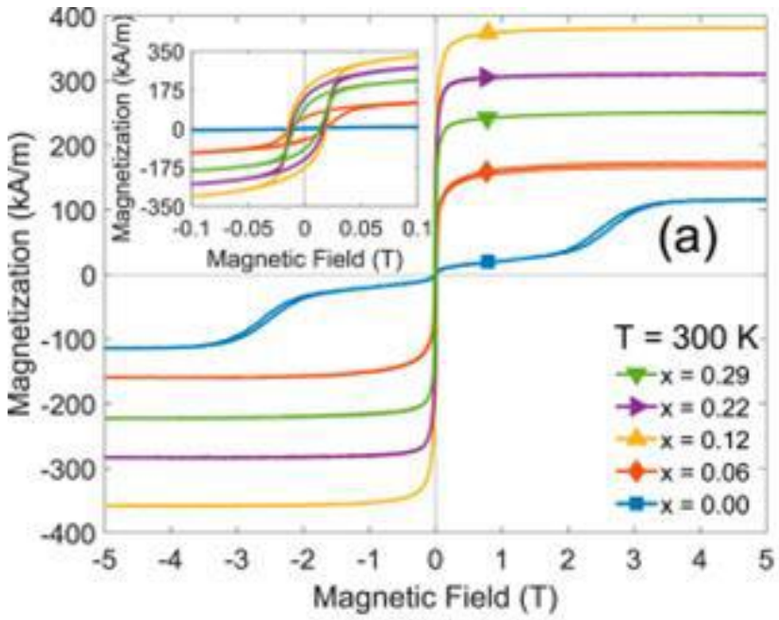
By partial substituting Mn with Cr on the M-site in Mn_2GaC. The FM response is observed in $(Mn_{1-x}Cr_x)_2GaC$ with $0.06 < x < 0.29$ up to temperatures well exceeding RT (489 K).

With x = 0.12, the highest saturation magnetization of 1.25 μB/M-atom at 3 K and maintain 0.90 μB/M-atom at 300 K was obtained.

This is the first MAX phase, which shows strong FM at room temperature, with great scope for further tuning of its magnetic properties through compositional doping.

(a) Magnetic hysteresis loops for all the $(Mn_{1-x}Cr_x)_2GaC$ samples at 300 K. The sample with x = 0.00 refers to Mn_2GaC which has the distinctive metamagnetic transition, with increasing Cr content, a typical FM response is obtained. The inset shows a zoomed-in view of the hysteretic part of the loop, demonstrating a large remanent magnetization for all Cr containing samples. All the measurements had the substrate MgO background subtracted.

(b) Remanent magnetization as a function of temperature for the sample series. The inset shows a zoomed-in view of the critical temperature region. Samples with x =0.12 and above show a typical ferromagnetic behavior, and the magnetization is largest for x = 0.12.



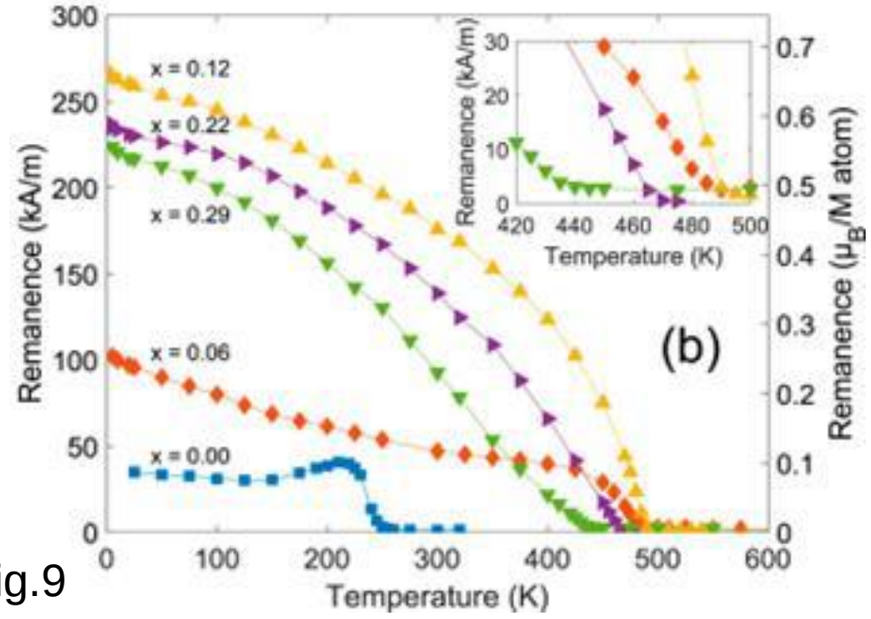


Fig.9

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Proposed studies

To fully understand the magnetic and structure system of the material, we need to use ^{57}Mn and ^{119}In eMS to perform

- Low and high temperatures measurements (~4 h per sample)
- Rotation measurement at RT with and without magnetic field parallel and perpendicular to the surface (1.5 h per sample per external field, 6.5 h total per sample)
- Rotation/Magnetic measurement at low temperatures (~2 h per sample).

Complete characterization with ^{57}Mn eMS is therefore expected to be around 9.5 hours per sample. Two samples, Mn_2GaC, $(Mn_{0.88}Cr_{0.12})_2GaC$, and one additional composition depending on the results will be investigated first. Then externed to other magnetic MAX phases such as rare earth elements (RE) doped on the M-site compounds. We will apply the ^{119}In to the samples which the ^{57}Mn data suggests importance to get data.

Together with calibration (10%) and contingency/further exploration of opportunity science (20%), we will need min. 4.5 Mn and 2.5 In shifts.

Measurement Plans

- Full temperature series to study the structural-magnetic phase transition in MAX phase Mn_2GaC and $(Mn_{0.88}Cr_{0.12})_2GaC$ thin films with ^{57}Mn and ^{119}In beam

  Hot lid: RT, 400 K, 500 K, 600 K
  Cold lid: RT, 250 K, 186 K, 175 K, 115 K, 103 K

- RT and or low temperature measurements with external magnetic field to study the field induced a magneto-structural transition in Mn_2GaC thin films with ^{57}Mn and ^{119}In beam.

- Rotation lid with or without an applied magnetic field to study magnetocrystalline anisotropy in Mn_2GaC and $(Mn_{0.88}Cr_{0.12})_2GaC$ thin films with ^{57}Mn beam and ^{119}In beam.

Summary of requested shifts

Beam	Min. Intensity	Energy	Target/Ion source	Samples	Shifts
^{57}Mn	$1.5 \cdot 10^{8}$ ions/s	≥50 keV	UC_2/RILIS	Mn_2GaC $(Mn_{1-x}Cr_x)_2GaC$ (x=0.12…)	4.5
^{119}In	$1.5 \cdot 10^{8}$ ions/s	≥50 keV	UC_2/RILIS	Mn_2GaC $(Mn_{1-x}Cr_x)_2GaC$ (x=0.12…)	2.5

Conclusions/Outlook

Considering the possibility to tune the magnetic properties through atomic substitution, doping, introduction of strain, temperature, and external magnetic field to optimize different functionalities of these thin films, further study on the local lattice structure and element-correlated magnetic properties is required to elucidate the delicate nature of the magnetic structure and to understand the non-trivial magnetic interactions in these exotic magnetic MAX phase thin films.

In this regard, the Mössbauer effect by the $^{57}Fe/^{119}Sn$ sites following implantation of radioactive ^{57}Mn and ^{119}In at various temperature can be used to probe the micro-structure and the site-related magnetism of the MAX phases with the Mn_2GaC-based thin films as protocol samples.

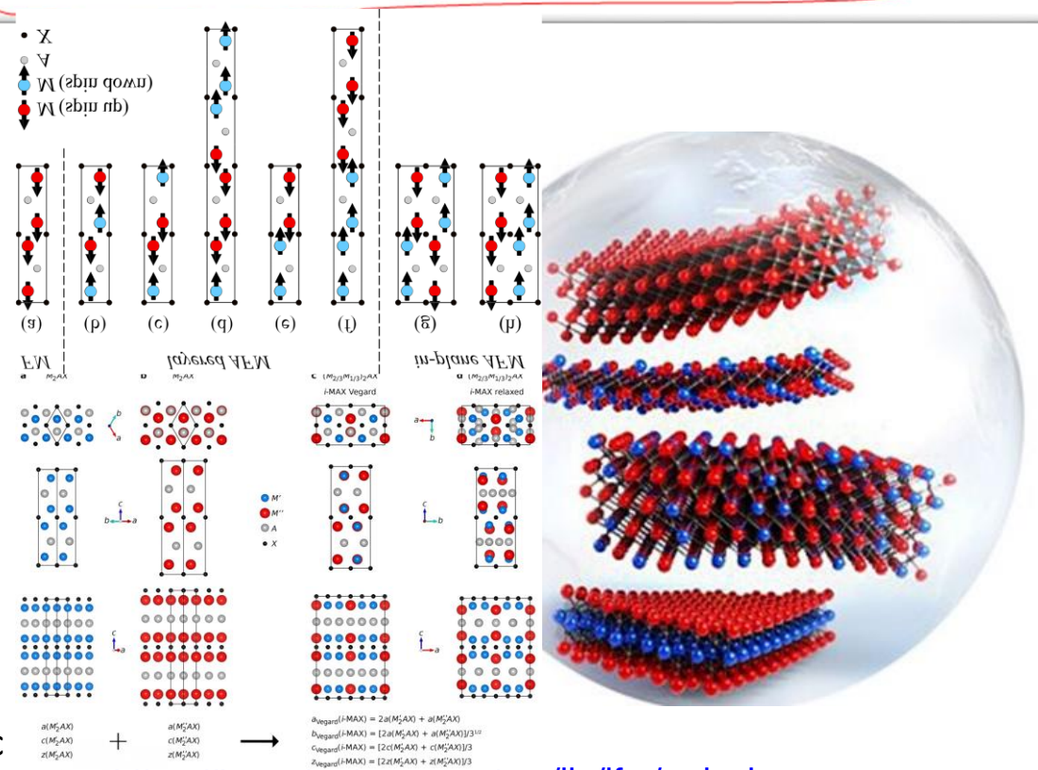
Our first attempt to study the MAX phase with eMS in 2023 has proved that the MAX phase is suitable for eMS studies using implantation.

What can be obtained

How far can we push the design and tailoring of materials properties for new applications? This ultimately depends on the control of atomic constituents while composing and structuring a material.

To explore the range of attainable properties, we need to increase the fundamental understanding of the materials and the synthesis processes in which they form, on an atomistic level.

- Gain the first-hand information of the site-specific magneto-structural phase transition properties of the MAX phase Mn_2GaC-based thin films in a full temperature range, up to their Curie temperatures.
- Document the changes in the nature of the probe site at low temperatures, both with respect to magnetic interaction and the local site structure properties.
- Use the above experimental methods to explore the effect of compositional doping on the magnetic and structural properties of the other complex magnetic MAX phase materials.
- A direct correlation between the local structure and the rich magnetic phase diagram (and other physical or electrical properties) of the MAX phase thin films could be established, and externed to study the new interesting magnetic MAX phases such as rare earth elements (RE) doped on the M-site compounds.



https://liu.se/en/organisation/liu/ifm/mdesign

A. Ingason et al. J. Phys.: Condens. Matter 28 (2016) 433003
M. Dahlqvist et al. Nanoscale, 14(2022) 10958-10971

Complementary research

- Besides the existing XRD, TEM on crystal structure characterization, VSM, NR, NMR studies on the magnetic properties,

- Temperature induced crystal structure changes in phase transition can be followed by the X-Ray diffraction facilitated with in-situ annealing at our home institute in Iceland.

- DFT and Wien2k theoretical calculations can be performed by the experts within our eMS collaboration group and by Prof. J. Rosen group in Sweden.

- Wide range of high structure quality thin films of the new magnetic MAX phases can be fabricated in our lab in Iceland and with Prof. J. Rosen group in Sweden.

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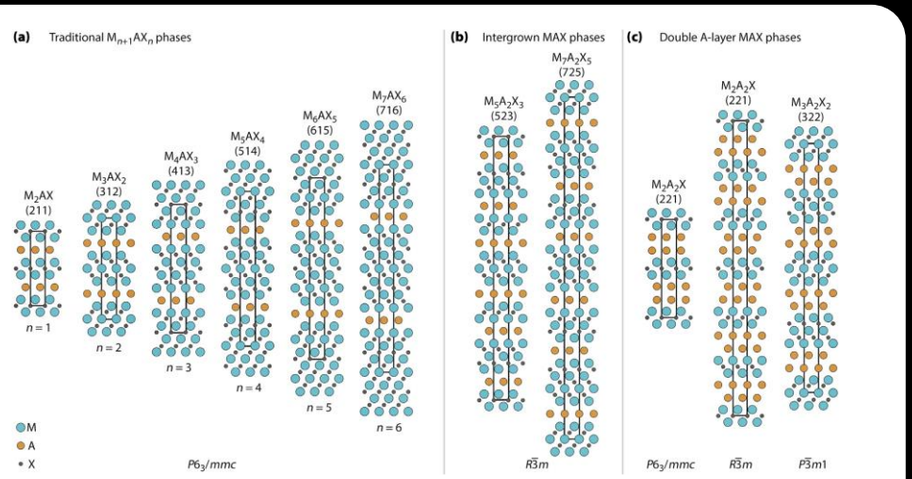

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