Report on experiment HC-5023 on beamline ID 12, 02-07 November 2022

**Coupling of Magnetic Layers in $(Cr_{1-x}Mn_x)_2GaC$ MAX phases investigated by the combination of XLD and XMCD**


## Abstract

The aim of the study is the understanding of magnetic coupling and resulting electronic changes in the atomically-layered magnetic $(Mn_{1-x}Cr_x)_2GaC$ MAX phase system. Due to complex non-collinear antiferromagnetic coupling driven by competing antiferromagnetic (AFM) and ferromagnetic (FM) interlayer exchange over the Ga layer, a rich phase diagram has been obtained. For $Mn_2GaC$, this is accompanied by huge magnetostriction (450 ppm in 3 T) with sign inversion at the 1st order phase transition around 220 K. Substituting Cr for Mn weakens the interlayer coupling resulting in reduced ordering temperatures from about 500 K for $Mn_2GaC$ to about 200 K for $(Mn_{0.5}Cr_{0.5})_2GaC$ and already moderate external fields (0.3 T) can break the AFM coupling between FM ordered (Mn,Cr)-C-(Mn,Cr) sheets. Laboratory-based structural and magnetic studies have risen the hypothesis that the coupling depends on the local Mn environment which should be addressed by hard X-ray Linear Dichroism (XLD) and XMCD.


## Samples

In total, we investigated 8 epitaxial thin films samples prepared by pulsed laser deposition (PLD) and direct-current magnetron sputtering (DCMS). The growth of $(Cr_{1-x}Mn_x)_2GaC$ MAX phase (symmetry Pm-3m) thin films on MgO(111), $Al_2O_3$(001), muscovite(001) was carried out in ultra-high vacuum (base pressure < $1{\cdot}10^{-8}$ mbar). Two additional films were grown magnetron sputter epitaxy. A $Mn_3GaC$ antiperovskite film with cubic symmetry was prepared as a reference by solid state reaction at 500 °C for 12h starting from a PLD-grown $[Mn_3Ga(0.7Å)/C(0.7Å)]_{550}$ multilayer stack on MgO(111) substrate. All films were characterized in our home laboratory by XRD, SEM-EDX and XPS. Table 1 gives an overview covering Mn contents of 13%-100% in $(Cr_{1-x}Mn_x)_2GaC$.

*Table 1. Chemical composition, crystal structure and thickness of $(Cr_{1-x}Mn_x)_2GaC$ thin films, APV, DCMS, PLD stand for antiperovskite, direct-current magnetron sputtering and pulsed laser deposition, respectively.*

| # | Chemical composition (at.%) | Texture and | Crystal structure | Substrate used | d, nm | Chemical treatment | Preparation method |
|---|---|---|---|---|---|---|---|
| $\mathbf{M}_o^{13}$ | $(Cr_{0.87}Mn_{0.13})_2GaC$ | MAX(001) | ($P6_3/mmc$) | MgO(111) | 75 | no | PLD |
| $\mathbf{M}_{o.e}^{15}$ | $(Cr_{0.85}Mn_{0.15})_2GaC$ | MAX(001) | ($P6_3/mmc$) | MgO(111) | 75 | HCl 11 min | PLD |
| $\mathbf{M}_o^{35}$ | $(Cr_{0.65}Mn_{0.35})_2GaC$ | MAX(001) | ($P6_3/mmc$) | MgO(111) | 51 | no | PLD |
| $\mathbf{M}_o^{50}$ | $(Cr_{0.50}Mn_{0.50})_2GaC$ | MAX(001) | ($P6_3/mmc$) | MgO(111) | 80 | no | DCMS |
| $\mathbf{M}_m^{54}$ | $(Cr_{0.46}Mn_{0.54})_2GaC$ | MAX(001) | ($P6_3/mmc$) | muscovite(001) | 52 | no | PLD |
| $\mathbf{M}_s^{67}$ | $(Cr_{0.33}Mn_{0.67})_2GaC$ | MAX(001) | ($P6_3/mmc$) | $Al_2O_3$(001) | 55 | no | PLD |
| $\mathbf{M}_o^{100}$ | $Mn_2GaC$ | MAX(001) | ($P6_3/mmc$) | MgO(111) | 100 | no | DCMS |
| $\mathbf{A}_o^{100}$ | $Mn_3GaC$ | APV(111) | (Pm-3m) | MgO(111) | 40 | no | PLD |

**Experiments**

X-ray absorption spectra for the Mn K-edge, Cr K-edge and Ga K-edge were collected on beamline ID12 in fluorescence yield (FY) mode. Polarization-dependent X-ray absorption, X-ray linear dichroism (XLD), and X-ray magnetic circular dichroism (XMCD) experiments were performed. The X-ray fluorescence signal from the samples was collected in the backscattering geometry, using Si photodiodes. The XLD signal is obtained as the difference between two absorption spectra measured with the X-ray polarization vector being either parallel and nearly perpendicular (80°) to the sample normal at 300 K. The installed X-ray quarter-wave plate allowed us to transform the incoming circularly polarized beam into two orthogonal linearly polarized beams at each energy point of the scan. The local magnetic properties of the Mn and Ga sites were studied using XMCD at the Mn and Ga K edge. Measurements were performed in ±5 T at 100 K at grazing incidence (15°). Element-selective magnetization on Mn and Ga were recorded by monitoring the intensity of the XMCD signal as a function of an applied magnetic field.

As an attempt to measure magnetostriction, XLD spectra at the Mn K-edge at 100 K and grazing incidence of 15° for $Mn_2GaC$ MAX phase film ($M_o^{100}$ sample) were done as function of the field (0, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, 3, 4, 5 Tesla). As a control, we measured XLD on the $Mn_3GaC$ reference sample under identical conditions which - as expected – shows no linear dichroism. Measurement of XMCD spectra at Mn and Ga K-edges were carried at 100 K at ±5 Tesla for $Mn_2GaC$ MAX phase film. XMCD field dependent curve were measured in the range of -5…5 Tesla.

XMCD spectra at Mn and Ga K-edges were carried at 170 K and ±7 Tesla for $Mn_2GaC$ MAX phase and $Mn_3GaC$ antiperovskite structures XMCD field dependent curve were measured in the range of -5…5 Tesla.

**Results**

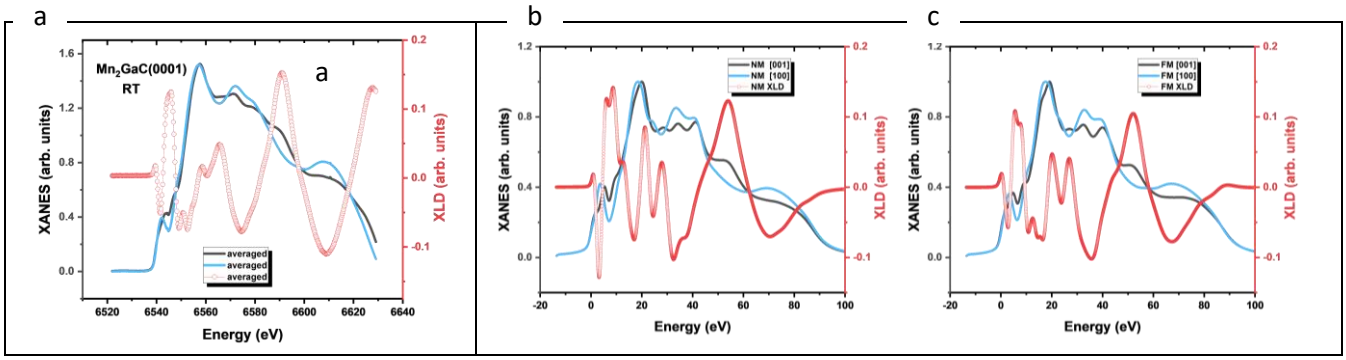


*Figure 1. (a) averaged XANES and XLD experimental spectra the $Mn_2GaC$ MAX phase. XANES and XLD calculated spectra for (b) spin-unpolarized and (c) spin-polarized $Mn_2GaC$ MAX phase.*

Various sample adjustment procedures were carried out to define diffraction-free conditions for the XANES measurement. This included measurements at different grazing incidence angles (12, 15, 20, 25 degrees). Resulting XLD spectra are not significantly affected. Mean XANES and XLD spectra for $Mn_2GaC$ film are presented in Figure 1(a). The XLD spectrum reveals various extrema indicating a highly anisotropic MAX-phase structure which is in a good correspondence to a density functional theory-based spectrum (CASTEP) of $Mn_2GaC$ in a spin-

polarized state in Figure 1(c) while the unpolarized calculated spectrum reveal a significantly different spectral signature, i.e. at 13 eV above the edge.

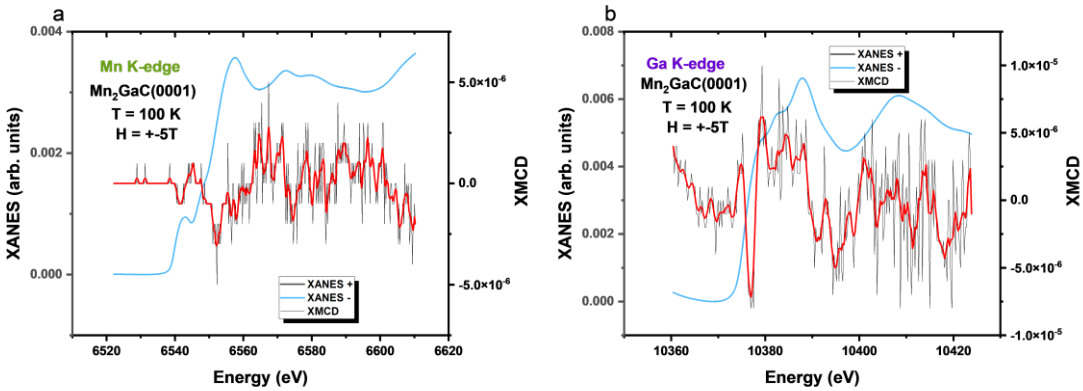


*Figure 2. XANES and XMCD experimental spectra measured at magnetic field of ±5 T at 100 K for sample* $\boldsymbol{M_o^{100}}$ *($Mn_2GaC$ MAX phase) at (a) Mn K-edge and (b) Ga K-edge.*

The Mn K-edge XMCD and XANES spectra are shown in Figure 2 (a). The XCMD spectra in $Mn_2GaC$ are denoted by black and red solid lines (smoothed). The XANES spectra indicate that these compounds are metallic. The dichroic signal is about $10^{-3}$ to relative to the XANES spectra. In $Mn_2GaC$, the XMCD spectrum at Mn K-edge is characterized by a dispersion type profile having a positive peak at 3 eV above the edge and negative one at 11 eV. In turn, the Ga K-edge XMCD spectrum shows a well-pronounced peak on the edge.

**Summary**

The beamtime experiment HC-5023 was very successful. We collected XLD data for a series of MAX phase $(Cr_{1-x}Mn_x)_2GaC$ heteroepitaxial thin films for x = of 0.13 - 1 deposited on MgO(111), Al2O3(0001) and KAl3Si3O10(001) substrates by pulsed laser deposition and magnetron sputtering at T = 500-600 °C. X-ray absorption near edge spectroscopy (XANES) spectra were collected at the Mn K-edge, Cr K-edge and Ga K-edge. Evidence of chemical disorder associated with (Mn, Cr) is observed. The similarity of the Cr K-edge spectra to Mn, and the presence of a strong X-ray linear dichroism signal for the Mn K-edge, indicates that Mn is substitutional for Cr in the MAX phase hexagonal lattice. With increasing Mn content additional features attributed to a cubic antiperovskite structure are observed. Simulations of the XANES spectra confirm the origin of X-ray linear dichroism observed in the sample, which is due to the inherent nanolaminated structure of the MAX phase.

Overall, the beamline ID12 of the ESRF allowed us to measure the angular-dependent spectroscopic features and correlate these to the anisotropic structure of the MAX phases and as function Mn content at highest quality by the combination of XANES, XLD and XMCD . The possibility of measuring in large fields and variable temperatures was important addressing the above research question. The end stations at ID12 fully supported such investigations. The detailed analysis is ongoing, and we aim for publication of the results till summer 2023.