2023 IEEE International Magnetic Conference - Short Papers (INTERMAG Short Papers) | 979-8-3503-3836-2/23/$31.00 ©2023 IEEE | DOI: 10.1109/INTERMAGShortPapers58606.2023.10228222

$Mn_{4-x}Ga_xN$ Thin Films for Ferrimagnetic Spintronics

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Ferrimagnetic compensation in $Mn_{4-x}Ga_xN$ (0<x<0.27) thin films grown by sputtering on (001) MgO is determined from magnetisation and Anomalous Hall effect measurements and compared with results on the bulk material. Compensation appears in films with x >0.15 and it occurs at 235 K when $x = 0.18$. A greater amount of Ga-doping is required to achieve compensation in the bulk, where room-temperature compensation is at $x = 0.26$. The differences are discussed in terms of Ga site occupancy in the Mn_4N structure, and an effect of the change of easy axis of the triangular ferrimagnetic spin structure from [111] in the bulk to [001] in the tetragonally-distorted films.

***Index Terms*—Anomalous Hall effect, Compensated Ferrimagnet, $Mn_{4-x}Ga_xN$ thin films, Non-collinear spin structure**

I. Introduction

Bulk Mn_4N is a ferrimagnetic material where Mn has an fcc structure with N in the 1b body centre interstitial site. The Mn 1a corner sites and Mn 3c face center sites are then inequivalent. The compound orders ferrimagnetically in a triangular structure with a [111] easy axis, where the 1a sublattice moments lie along the axis, but the three 3c spins are noncollinear [1]. The 3c sites form a magnetically frustrated kagome lattice, because the nearest-neighbour Mn-Mn coupling is antiferromagnetic. The component of each 3c moment along [111] is opposite to the 1a moment, and their components perpendicular to [111] are at 120° to each other, forming a triangular or 'umbrella' spin structure illustrated in Fig 1 (a). According to recent DFT calculations [2], the 1a and 3c Mn moments are 3.65 μ_B and 2.35 μ_B respectively, and the 3c moments make an angle $\theta = 70°$ with the [111] axis, giving a net moment of 1.24 μ_B/f.u.. Experimentally a value of 1.1 μ_B/f.u. is found [2]. 1a is the dominant sublattice at all temperatures below the Curie temperature of 780 K, and there is no ferrimagnetic compensation point.

Thin films of (001) Mn_4N are not quite the same. They exhibit perpendicular magnetic anisotropy (PMA), attributed to in-plane tensile strain [3]. The magnetic spin structure is clearly altered and He *et al.* proposed an appropriate structure, in Fig. 1 (b), that has PMA, retains a non-collinear component on the Mn 3c sites and respects the signs of the distance-dependent Mn-Mn exchange interactions [4]. Their suggestion was based on spin structures determined experimentally for different bulk Mn_3ZN metallic perovskites, where Z = Cu and Rh. Again there is no compensation at any temperature, but the net moment is only 0.52 μ_B/f.u. at 300 K, and the 1c and 2e sublattices now make different angles with the easy axis.

It has been shown that by doping bulk Mn_4N with elements which replace Mn 1a sites, compensation can be achieved. Zhang *et al.* concluded that Ga is the recommended dopant to use in terms of use in spintronics applications and compensation close to room temperature is achieved in $Mn_{4-x}Ga_xN$ for $x = 0.26$. Here we were motivated to study the magnetic and transport properties of a series of $Mn_{4-x}Ga_xN$ thin films and to understand whether we can make a composition which compensates close to room temperature.

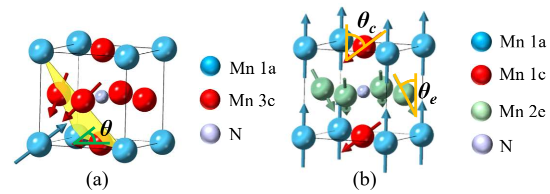

Fig. 1. Non-collinear spin structure of (a) bulk and (b) thin film forms of Mn_4N. The yellow triangle in (a) is the (111) plane. Angles θ, θ_c and θ_e are highlighted [2], [4].

II. Methodology

Epitaxial $Mn_{4-x}Ga_xN$ thin films were grown on single side polished (100) MgO substrates by reactive magnetron sputtering. The films were co-sputtered from Mn and Mn_3Ga targets (all with 2N5 purity) in the presence of N_2 with a N_2:Ar ratio of 1:20. N_2 was also present as the sample cooled down after the deposition. For each composition, the deposition parameters were adjusted such that the correct phase was achieved. The quality of films was particularly affected by the flow rate of N_2 into the chamber during the cooling down stage, S_{N_2}. See Table I for details. X-ray diffraction and reflectivity measurements were carried out on a Panalytical X'Pert Pro diffractometer with Cu Kα source. Room temperature Anomalous Hall Effect (AHE) measurements were performed in a 2 T GMW electromagnet. All thin films were magnetically characterised using a 5 T Quantum Design SQUID magnetometer.

TABLE I
Deposition temperature T_{dep}, S_{N_2} and sample thickness, t.

Composition	T_{dep} (°C)	S_{N_2} (sccm)	t (nm)
Mn_4N	440	2.6	33.1
$Mn_{3.90}Ga_{0.10}N$	440	2.3	33.2
$Mn_{3.88}Ga_{0.12}N$	425	2.1	26.3
$Mn_{3.87}Ga_{0.13}N$	425	2.3	27.5
$Mn_{3.85}Ga_{0.15}N$	390	2.4	23.9
$Mn_{3.82}Ga_{0.18}N$	410	1.6	33.4
$Mn_{3.80}Ga_{0.20}N$	390	1.9	30.0
$Mn_{3.73}Ga_{0.27}N$	390	1.5	38.2

† $Mn_{3.73}Ga_{0.27}N$ contains traces of $\alpha-$Mn.

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III. Results & Discussion

Figure 2 is a plot of the Anomalous Hall resistivity ρ_{xy} as a function of applied magnetic field at room temperature for a set of $Mn_{4-x}Ga_xN$ films. The loop for pure Mn_4N, in red, is the only one that saturates fully, with a coercivity of 0.28 T. The coercivity increases with increasing x but the film with $x = 0.18$ is impossible to magnetise in 2 T, which shows the coercivity is diverging because it is close to compensation. It was shown that dopant Ga atoms replace the corner 1a Mn atoms in bulk material [2]. Therefore as x increases, there comes a point where the net magnetisation of the Mn 3c sublattices exceeds that of the 1a sublattice and the sign of the AHE loop changes. The film with $x = 0.18$ is very close to compensation while that with $x = 0.20$ is above compensation at 300 K and can be magnetised (but not saturated) in 2 T. The Mn 3c sublattices are now clearly dominant. A big difference between bulk and thin film $Mn_{4-x}Ga_xN$ is that room-temperature compensation is found at $x = 0.26$ in the bulk [2], but for thin films it is just below $x = 0.18$.

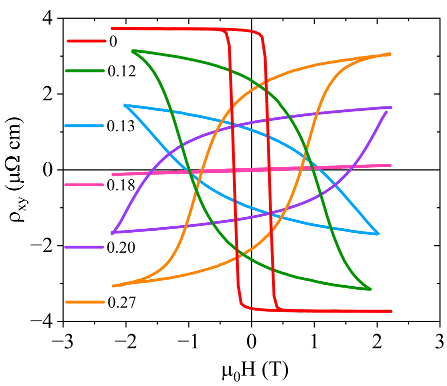

Fig. 2. Hall resistivity for a series of $Mn_{4-x}Ga_xN$, the value of x is noted.

Curves of remanent magnetisation M_r versus temperature are shown in Fig. 3. No films with $x \leq 0.15$ compensate below 400 K, while $x = 0.18$ compensates at 235 K. The increase of M_r with increasing temperature for $x = 0.20$ and 0.27 indicates that the average angle of the fcc sublattice spins with [100] tends to decrease with increasing temperature. The coercivity of both SQUID and AHE loops at room temperature is plotted as a function of x in Fig. 4. Values for the AHE minor loops are estimates. The SQUID loops for all except $x = 0$ show a soft component (see inset of Fig. 4 for $x = 0.13$), which is absent in the AHE loops, and is therefore somehow associated with the non-collinear sublattices. The value of coercivity is deduced from the hard component of the SQUID loops, as shown by the purple dashed lines in the inset. The exact origin of the wasp-waisted shape is currently unknown. The dashed green lines at $x = 0.15$ and 0.18 along with the red arrows indicate that the coercivity of these loops is much greater than the 5 T maximum of our SQUID. The field of 2 T was not enough to saturate most of the AHE loops, thus there are fewer coercivity points for the ρ_{xy} data.

Since the room-temperature coercivity of $Mn_{4-x}Ga_xN$ thin films diverges between $x = 0.15$ and 0.18, compensation lies in this range, probably close to $x = 0.17$, compared

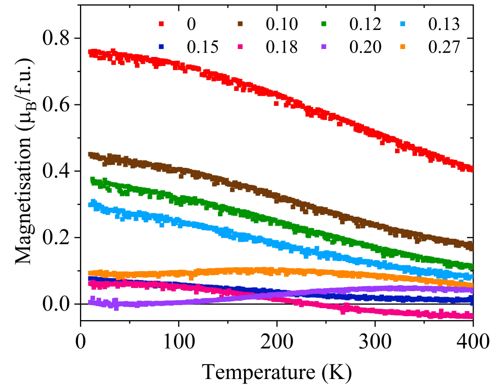

Fig. 3. M_r versus temperature. All curves were recorded after saturating the magnetisation in 5 T and heating in zero field.

to $x = 0.26$ in the bulk. The difference can be associated with the smaller ground state ferrimagnetic moment in the pure films, 0.52 μ_B/f.u. compared to 1.1 μ_B/f.u. in the bulk. The magnitudes of the Mn atomic moments are unlikely to be significantly altered by the 1% tetragonal distortion, so the difference is best explained by a closing of the umbrella, to an average angle of 64° for the face centre sites. There might also be a different fraction of Ga on the 1a sites in the films but there are too few X-ray reflections to confirm this.

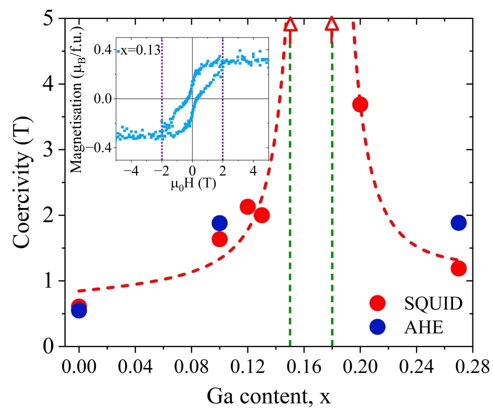

Fig. 4. Coercivity from SQUID (red) and AHE (blue) measurements plotted as a function of Ga-doping, x. The dashed red line is a guide.

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Acknowledgements

This work was supported by SFI under the MANIAC, SFI-NSF China Project (Grant No. 17/NSFC/5294) and the FFP grant FISTMAP (21/FFP-P/10175). Lucy Prendeville is funded by the IRC under grant GOIPG/2019/4430.