EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Charge states of transition metal ions and local magnetic structure of dilute magnetic semiconductor (Ga,Fe)N:Mn – an emission Mössbauer spectroscopy study

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Abstract

From previous ^{57}Fe/^{57}Mn eMS studies on epitaxial layers of Mn doped AlGaN, GaN and InGaN at ISOLDE, a wealth of information has been obtained on the charge state and interactions of Fe with dopants (experiments IS630 and IS576). Here we want to make use of the renewed interest in Fe and Mn co-doped GaN, (Ga,Fe)N:Mn where the formation or suppression of iron nitride precipitates can be controlled with appropriate doping/annealing thereby tuning between a dilute magnetic semiconductor and a condensed magnetic semiconductor. Using the knowledge obtained from previous eMS studies, we will follow the state of implanted Mn/Fe to predict the effects of doping on the charge/spin state of the probe atoms and the mechanism leading to precipitation and/or suppression of precipitation.

Requested shifts: 12 shifts split into ~3 runs over ~2 years

1. MOTIVATION

Transition metal (TM) doped III-nitrides have been studied extensively over the last decade as workbench for semiconductor spintronics [1-22]. In particular, depending on the growth conditions, the introduction of magnetic ions in III-nitrides result in: (i) a dilute homogeneous system [10], (ii) a chemically inhomogeneous phase separated system [19,22], (iii) a crystallographically inhomogeneous system [22], (iv) a system hosting magnetic and optical complexes [13]. Among the TM doped III-nitrides, epitaxial layers of Fe doped GaN also attracted significant attention as magnetic semiconducting systems [5,6,8,9]. While (Ga,Fe)N with Fe ions concentration <0.4% is dilute, homogeneous and predominantly paramagnetic, crystallographic phase separation occurs for higher Fe contents in the wurtzite GaN matrix, leading to the self-assembleing of ferromagnetic iron nitride nanocrystals (NCs) embedded in the GaN matrix [1,2,4,8]. The magnetic properties of these Fe_xN phases depend on the concentration of N atoms. The N-poor phases such as γ'-Fe_4N, γ'-$Fe_{4-x}Ga_xN$ and ε-Fe_3N have been shown to be ferromagnetic [5,6]. A nitride semiconducting matrix embedding ferromagnetic NCs can pave the way to the realization of the next generation of spin devices based on III-nitrides, in which the NCs can act as spin-polarized current injectors into the host matrix, leading to energy efficient devices such as spin batteries [18-20].

Epitaxial layers of dilute (Ga,Fe)N and (Ga,Mn)N with Fe and Mn concentrations ~0.4 % and ~3.1% are electrically insulating due to the lack of free charge carriers [1,2,4,8]. Dilute (Ga,Fe)N has been shown to exhibit paramagnetism, while the ferromagnetism in (Ga,Mn)N for Mn concentrations between 1% and 10% was demonstrated to be mediated *via* a superexchange mechanism in absence of free charge carriers [1,12,14,17]. Co-doping of (Ga,Mn)N with the non-magnetic acceptor and dopant ions Mg and Si, respectively, results in the formation of Mn-Mg_k and Mn-Si_k complexes that allow the control of charge state and of spin state of Mn^{n+} in the range $3 \leq n \leq 5$ and $2 \geq S \geq 1$, where S is the spin state [13]. These complexes were shown to be optically active in the infrared (IR) range of the electromagnetic spectrum, thereby opening up to applications in IR optoelectronics, in particular as indium free laser diodes and light emitting diodes. The co-doping of (Ga,Fe)N with Mg and Si suppresses the formation of the Fe_xN NC phases even for Fe concentrations >0.4%. In both (Ga,Fe)N and (Ga,Mn)N, the co-doping with the non-magnetic acceptor and donor ions does not contribute free charge carriers and hence does not promote ferromagnetism in these dilute magnetic systems [13].

The effect of magnetic co-doping of III-nitride systems is however, still an open question. *Ab initio* electronic structure calculations predicted ferromagnetism in Mn, Cr [23] and Mn, V [24] co-doped dilute GaN systems. However, experimental reports on dilute systems of GaN co-doped with two magnetic species are not available to the best of our knowledge. Self-assembled γ′-Fe_4N NCs doped with Mn and embedded in a GaN matrix were reported by this group and the incorporation of Mn was shown to decrease the strength of ferromagnetism in the condensed magnetic system. Hence, the effect of Mn on the magnetic properties, on the local magnetic structure, on the crystallographic microstructure, on the charge and spin states of Fe and on the interplay of defects and disorder in epitaxial layers of (Ga,Fe)N studied *via* temperature, magnetic field and angle dependent emission Mössbauer spectroscopy is foreseen to provide insight into the magnetic co-

doping of III-nitrides, key for their design as functional dilute magnetic systems (DMS) for applications in spin driven devices.

2. SAMPLES AND METHODS

2.1 (Fe,Mn) co-doped GaN

The samples are grown by the QMag group, Johannes Kepler University, Linz in an AIXTRON 200RF horizontal tube metalorganic vapor phase epitaxy (MOVPE) reactor and deposited on *c*-plane sapphire (Al_2O_3) substrates using trimethylgallium (TMGa), bis-methylcyclopentadienyl-manganese ($MeCp_2Mn$), ferrocene (Cp_2Fe), and ammonia (NH_3) as precursors for Ga, Mn, Fe and N respectively, with H_2 as the carrier gas. Following a high temperature desorption of the epi-ready sapphire substrates, a low temperature GaN nucleation layer is grown at 540°C. The nucleation layer is then annealed at 1040 °C and followed by the growth of 1 µm-thick GaN buffer layer. A layer of (Ga,Fe)N:Mn of thickness 400 nm is then be deposited on the GaN buffer. The concentrations of the Fe and Mn ions is tuned and controlled by adjusting the flow of the $MeCp_2Mn$ and Cp_2Fe precursors.

The samples are thoroughly characterized *via* high resolution x-ray diffraction (HRXRD), high resolution transmission electron microscopy (HRTEM), secondary ion mass spectroscopy (SIMS), elastic recoil detection analysis (ERDA), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), superconducting quantum interference device (SQUID) magnetometry, electron paramagnetic resonance (EPR), ferromagnetic resonance (FMR) and low-*T*-high-*H* magneto-transport.

3. PRELIMINARY WORKS

In a recent publication, emission Mössbauer spectroscopy (eMS) was employed to investigate the charge states of Mn and Fe in epitaxial layers of $Al_xGa_{1-x}N$:Mn [21]. The results demonstrated that co-doping promotes the co-existence of unusual charge states of Fe^{4+} and Mn^{2+}, whereas their trivalent charge states prevail with either transition metal incorporated independently in III-

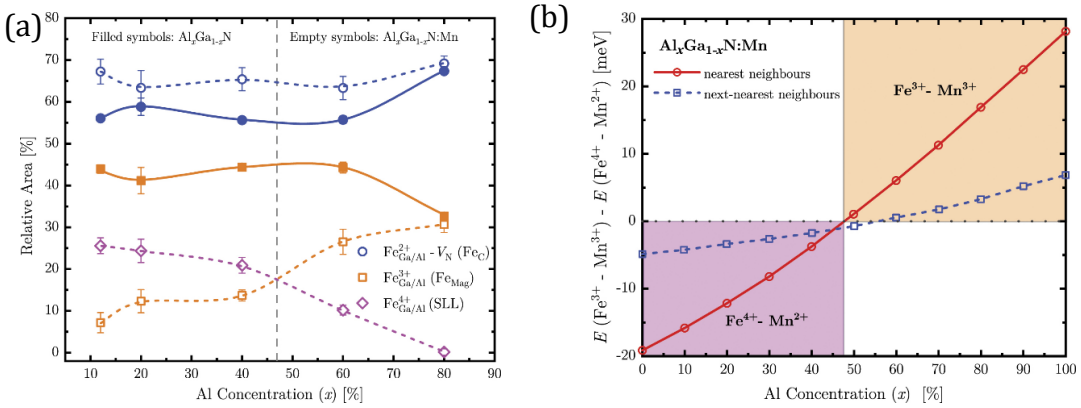

Fig. 1 (a): Relative area fractions at RT as a function of concentration (x) for $Al_xGa_{1-x}N$ (filled symbols) and $Al_xGa_{1-x}N$:Mn (empty symbols). The solid and dashed lines are guides to the eye. (b): Formation energy difference between Fe^{3+}–Mn^{3+} and Fe^{4+}–Mn^{2+} configuration as a function of x in $Al_xGa_{1-x}N$:Mn. Solid (dashed) lines show the energy difference when Fe and Mn are nearest (next nearest) neighbors while the shaded areas show regions of stability for the corresponding configurations. [Adapted from Ref. 21]

nitrides and are shown in Fig. 1, where an unusual Fe^{4+} - Mn^{2+} charge state is detected for $x < 0.5$. In an earlier publication [9], it was reported that co-doping of (Ga,Fe)N with Mg and Si suppresses the formation of the FeN secondary phases even for Fe concentrations >>0.4%, . In Fig.2, HRTEM images of Mg and Si doped (Ga,Fe)N are shown where the non-magnetic codopants are found to suppress the formation of the FeN NC phases.

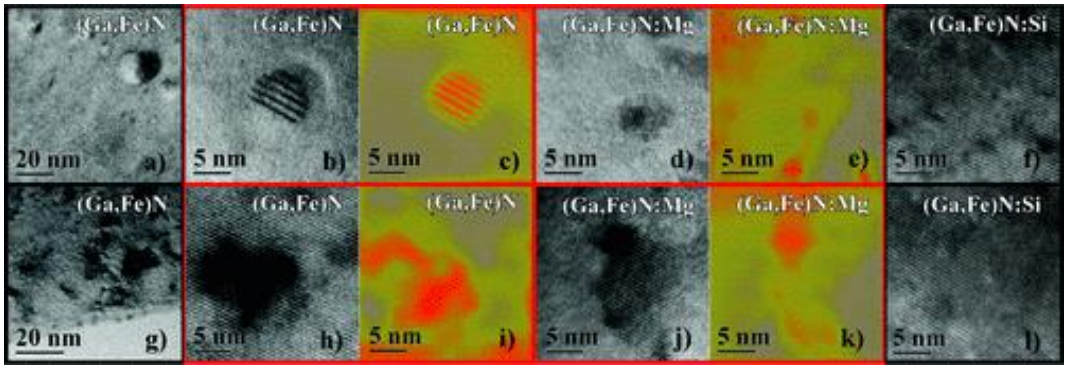

Fig. 2: Bright-field images (a),(g), TEM with mass contrast (b),(d),(f),(h),(j),(l), and Fourier filtered images with strain mapping (c),(e),(i),(k) of (Ga,Fe)N revealing the presence of Fe_3N precipitates (a)–(e), spinodal decomposition (g)–(k), and the effect of co-deposition of either Si (f),(l) or Mg (d),(e),(j),(k) preventing the formation of the Fe-rich regions.

4. EXPERIMENTAL PLAN AND BEAM REQUEST

The main objectives of the requested beam-time are:

(i) to determine the lattice site occupancy, the charge and the spin states of Mn and Fe ions in dilute (Ga,Fe)N:Mn;

(ii) to elucidate the effect of Mn on the suppression of segregation of Fe_xN NC phases in (Ga,Fe)N with Fe > 0.5%;

(iii) to identify the signatures of Fe_m-Mn_k magnetic complexes, if any, are formed for Mn, Fe co-doped GaN epitaxial layers.

through hyperfine interactions by employing eMS. The isotope proposed for implantation at ISOLDE is TM ^{57}Mn ($T_{1/2}$ = 1.5 minutes). The film thickness will be 400 nm. For each Fe concentration in (Ga,Fe)N, three different Mn concentrations will be co-doped. A total of **12 (Ga,Fe)N:Mn samples** will be studied in this project with the following Fe concentrations x_{Fe} and Mn concentrations x_{Mn} in the specimens:

Sample series	x_{Fe} (at. %)	x_{Mn} (at. %)
S1	0.1%	0.5; 1.0; 3.0
S2	0.4%	0.5; 1.0; 3.0
S3	1.0%	0.5; 1.0; 3.0
S4	2.0%	0.5; 1.0; 3.0

The experimental plan envisioned for the present proposal is aimed at in-depth eMS studies.

M.1: The first step will be to measure eMS spectra of the (Ga,Fe)N:Mn samples implanted with ^{57}Mn in the temperature range (100-600) K. Information on the annealing characteristics of the material, the hyperfine parameters and the site fractions as a function of temperature and the implanted isotope will be obtained. Further, the disorder induced by the implantation of the TM isotope can be quantified from the Mössbauer parameters, providing essential information on the magnetic properties and their correlation to the structural and electronic disorder induced in the system under investigation.

M.2: At every *T*, magnetic field and angular dependent eMS measurements will be conducted in order to determine the lattice position and the local magnetic properties of the ^{57}Mn implanted (Ga,Fe)N:Mn films.

5. SUMMARY OF REQUESTED SHIFTS

A total of 12 shifts are requested over 2 years. The requested shifts are summarized in the following table:

Sample series	Type of experiment	No. of requested shifts	Comments
S1	eMS (M1, M2)	3	Hot runs, angular dependences and cold runs
S2	eMS (M1, M2)	3	
S3	eMS (M1, M2)	3	
S4	eMS (M1, M2)	3	

6. COMPLEMENTRY RESEARCH

The eMS results, relevant in particular to the lattice site assignments, lattice distortions, vacancy mobility and Debye temperature estimations will be supported by *ab initio* density functional theory calculations done by Arthur Ernst at JKU Linz. The samples will be comprehensively characterized by HRXRD, HRTEM secondary ion mass spectroscopy (SIMS), elastic recoil detection analysis (ERDA), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) to study the structural and chemical composition. The bulk magnetic properties of the samples will be studied by employing SQUID magnetometry, *T* multifrequency EPR and FMR. Custom designed electric field dependent magnetic properties and magnetic properties at $T < 1$ K will be measured as a part of an ongoing collaboration between the QMag group and IFPAN, Warsaw. X-ray absorption spectroscopy, in particular, extended x-ray fine structure spectroscopy (EXAFS), x-ray absorption near edge spectroscopy (XANES) and DAFS will be carried out at the SOLEIL Synchrotron (in the frame of a long-term collaborative project currently running) on the as grown and eMS studied samples to obtain complementary data on the local structure of the samples.

As opportunistic science, Mg and Si co-dopants in (Ga,Fe)N:Mn will also be studied, within the available shifts, to understand the effect of acceptor and donor co-dopants on the charge/spin

states of Mn and Fe and on the local and bulk magnetic properties of the magnetic III-nitride system.

7. CONCLUSION/OUTLOOK

From the experimental activity outlined above, the following outcomes are expected:

(i) local magnetic structure of the Fe and Mn in epitaxial layers of magnetically co-doped (Ga,Fe)N:Mn;

(ii) first insights into the charge and spin states of Fe and Mn in epitaxial layers of magnetically co-doped (Ga,Fe)N:Mn;

(iii) correlation betweenlattice disorder, electronic disorder and magnetic fluctuations using hyperfine parameters, in particular measured in the superconducting state of a conventional *s*-wave superconductor in the presence of TM dopants.

(iv) probing the effect of Mn on the solubility limit of Fe in wurtzite GaN: the surfactant role of Mn on the segregation of Fe into FeN self-assembled NC phases;

(v) evidence and signatures of Fe_m-Mn_k magnetic complexes, if any formed in magnetically co-doped (Ga,Fe)N:Mn.

These outcomes of the eMS measurements on magnetically co-doped (Ga,Fe)N:Mn will result in:

1. a systematic study of the evolution of microstructure and magnetism in technologically important dilute magnetic system (Ga,Fe)N:Mn.
2. a guiding path towards the understanding of charge and spin states of Mn and Fe in (Ga,Fe)N:Mn.
3. the understanding of the physical mechanisms involving the magnetic co-doping of wurtzite GaN using Mn and Fe and its impact on the global magnetic properties of this unexplored DMS.

The anticipated results obtained in the proposed shifts are expected to provide valuable insights for future proposals and in-depth studies of magnetically doped GaN for applications in semiconductor spintronics and spin-orbitronics based on all nitride integrated and hybrid devices.

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1 Details for the Technical Advisory Committee

3.1 General information

Describe the setup which will be used for the measurement. If necessary, copy the list for each setup used.

☒ Permanent ISOLDE setup: GLM beam line

☒ To be used without any modification

☐ To be modified: *Short description of required modifications.*

☒ Travelling setup (*Contact the ISOLDE physics coordinator with details.*)

☒ Existing setup, used previously at ISOLDE: Emission Mössbauer Spectrometer from Ilmenau (eMIL).

☐ Existing setup, not yet used at ISOLDE: *Short description*

☐ New setup: *Short description*

3.2 Beam production

For any inquiries related to this matter, reach out to the target team and/or RILIS (please do not wait until the last minute!). For Letters of Intent focusing on element (or isotope) specific beam development, this section can be filled in more loosely.

- Requested beams:

Isotope	Production yield in focal point of the separator (/μC)	Minimum required rate at experiment (pps)	$t1/2$
Isotope 1 Isotope 2 Isotope 3	^{57}*Mn 1.5x10^{8} at/μC*	^{57}*Mn 1x10^{8} at/μC*	85.4 s

- Full reference of yield information (*yield database*)
- Target - ion source combination: UC_x with RILIS
- RILIS? (*Yes for element ^{57}Mn*)

  ☐ Special requirements: (*isomer selectivity, LIST, PI-LIST, laser scanning, laser shutter access, etc.*)

- Additional features?

  ☒ Neutron converter: (*for isotopes 1, 2 but not for isotope 3.*)

  ☐ Other: (*quartz transfer line, gas leak for molecular beams, prototype target, etc.*)

- Expected contaminants: Isotopes and yields
- Acceptable level of contaminants: By using RILIS, no significant contaminants are expected.
- Can the experiment accept molecular beams? No
- Are there any potential synergies (same element/isotope) with other proposals and LOIs that you are aware of? IS630, IS681, IS683, IS670.

3.3 HIE-ISOLDE

For any inquiries related to this matter, reach out to the ISOLDE machine supervisors (please do not wait until the last minute!).

- HIE ISOLDE Energy: *(MeV/u); (exact energy or acceptable energy range)*

  ☒ Precise energy determination required

  ☐ Requires stable beam from REX-EBIS for calibration/setup? *Isotope?*

- REX-EBIS timing

  ☒ Slow extraction

  ☐ Other timing requests

- Which beam diagnostics are available in the setup?
- What is the vacuum level achievable in your setup?

3.4 Shift breakdown

The beam request only includes the shifts requiring radioactive beam, but, for practical purposes, an overview of all the shifts is requested here. Don't forget to include:

- Isotopes/isomers for which the yield need to be determined
- Shifts requiring stable beam (indicate which isotopes, if important) for setup, calibration, etc. Also include if stable beam from the REX-EBIS is required.

An example can be found below, please adapt to your needs. Copy the table if the beam time request is split over several runs.

Summary of requested shifts:

With protons	Requested shifts

Yield measurement of isotope 1 Optimization of experimental setup using isotope 2 Data taking, isotope 1 Data taking, isotope 2 Data taking, isotope 3 Calibration using isotope 4	^{57}Mn -- 12 shifts
Without protons	Requested shifts
Stable beam from REX-EBIS (after run) Background measurement	0.5 shift for stable beam for every beam time with ^{135}Cs to GLM beam line: EqArr_2023_09_12_20_02_46_GLM-eMS-50kV_DP418_KI-520_135Cs.csv YGPS.BFC4900: 238 pA At least 90% of transmission expected at the Faraday cup of eMIL (traveling setup at the GLM beam line)

3.5 Health, Safety and Environmental aspects

3.5.1 Radiation Protection

- If radioactive sources are required:
  - Purpose? Online experiment with ^{57}Mn.
  - Isotopic composition? ^{57}Mn.
  - Activity? 300 MBq online with no manipulation. Manipulation with only 30 kBq according to the existing and approved procedure.
  - Sealed/unsealed? Unsealed.
- For collections:
  - Number of samples? **12**
  - Activity/atoms implanted per sample? 300 MBq online with no manipulation. Manipulation with only 30 kBq according to the existing and approved procedure.
  - Post-collection activities? Shipping

3.5.2 Only for traveling setups

- Design and manufacturing

  ☐ Consists of standard equipment supplied by a manufacturer

  ☒ CERN/collaboration responsible for the design and/or manufacturing ISIEC file of eMIL can be found at EDMS: 1317710.

- Describe the hazards generated by the experiment:

Domain	Hazards/Hazardous Activities		Description
Mechanical Safety	Pressure	☐	[pressure] [bar], [volume][l]
	Vacuum	☒	10^{-5} mbar
	Machine tools	☒	The alignment of eMIL with the GLM beam line requires the adjustment of the equipment height.
	Mechanical energy (moving parts)	☒	Stepping motor of four-positions lid.
	Hot/Cold surfaces	☒	Cold surface for liquid N_2 experiments. Hot lid does not cause hot surface.
Cryogenic Safety	Cryogenic fluid	☒	Liquid N_2 (approximately 4 liters per load)
Electrical Safety	Electrical equipment and installations	☒	Several devices, please consult the safety file EDMS 1317710 for details.
	High Voltage equipment	☒	Detector 1000 V DC with current being less than 1 nA.
Chemical Safety	CMR (carcinogens, mutagens and toxic to reproduction)	☐	[fluid], [quantity]
	Toxic/Irritant	☐	[fluid], [quantity]
	Corrosive	☐	[fluid], [quantity]
	Oxidizing	☐	[fluid], [quantity]
	Flammable/Potentially explosive atmospheres	☐	[fluid], [quantity]

	Dangerous for the environment	☐	[fluid], [quantity]
Non-ionizing radiation Safety	Laser	☐	[laser], [class]
	UV light	☐	
	Magnetic field	☒	0.6 T
Workplace	Excessive noise	☒	General ISOLDE hall background noise.
	Working outside normal working hours	☒	According to the ISOLDE schedule.
	Working at height (climbing platforms, etc.)	☐	
	Outdoor activities	☐	
Fire Safety	Ignition sources	☐	
	Combustible Materials	☐	
	Hot Work (e.g. welding, grinding)	☒	Measurements of samples using the hot lid (cold surface).
Other hazards	^{57}Mn (high energy beta emitter)		

Samples: The (Ga,Fe)N:Mn samples are not hazardous and pose no health issues. Also, the samples are stable at temperatures to be employed in this experiment and stable to radiation.