# Magnetization steps in dilute bulk GaN:Mn

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## GaN:Mn is even more important than ever before!

- It is foreseen to serve as a **highly resistive GaN substrate** indispensable for laterally operating electronic devices like high electron mobility transistors or high-power switches.
- At higher Mn concentrations **ferromagnetic form of GaN** may have an enormous technological relevance due to the already dominating role of the nitride family in the light industry, high-frequency, and high-power electronics. From practical point of view, the existence of sizable piezo-electromagnetic coupling in (Ga,Mn)N opens the door for realization of external electric field driven repeatable magnetization reversal [1].

The key factor is to kill native weak conductivity through numerous donor defects. To this end acceptors (Fe, C, Mn) need to be incorporated. Mn doping seems to be the most promising route since, for the same acceptor concentration, GaN:Mn crystals present better structural quality and higher resistivity than GaN:Fe [2].

To master the process of effective Mn doping a deeper understanding of the physics which governs the behavior and magnetic properties of Mn species in nitrides is very timely and important.

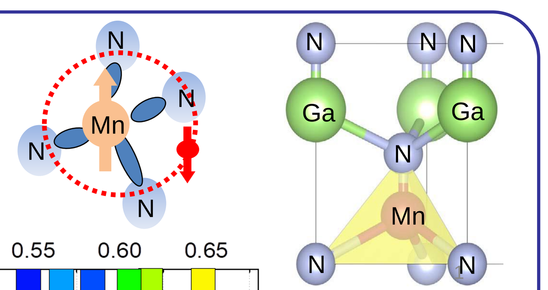
Our work exemplifies the wealth of material information which can be obtained from detailed magnetometry and EPR technique.

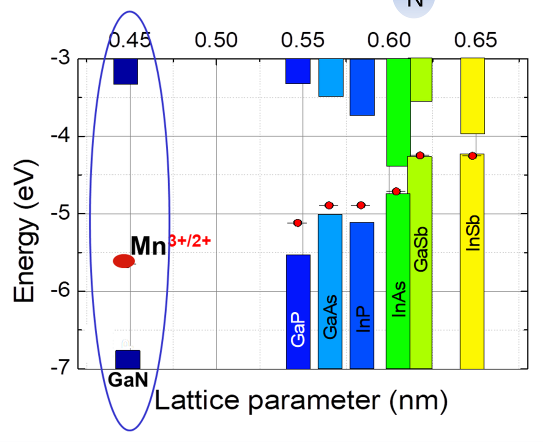
## Ga-subsitutional Mn acceptor in wurtzite GaN

✓ forms mid-gap $Mn^{2+}/Mn^{3+}$ ($A^-/A^0$) level (impurity band) [3-5]
➔ GaN:Mn excellent semi-insulating material (up to at least 10% of Mn)

✓ hole binding energy: mostly *p-d* hybridization [6]
➔ Zhang-Rice polaron; $Mn^{3+} = Mn^{2+} + h$

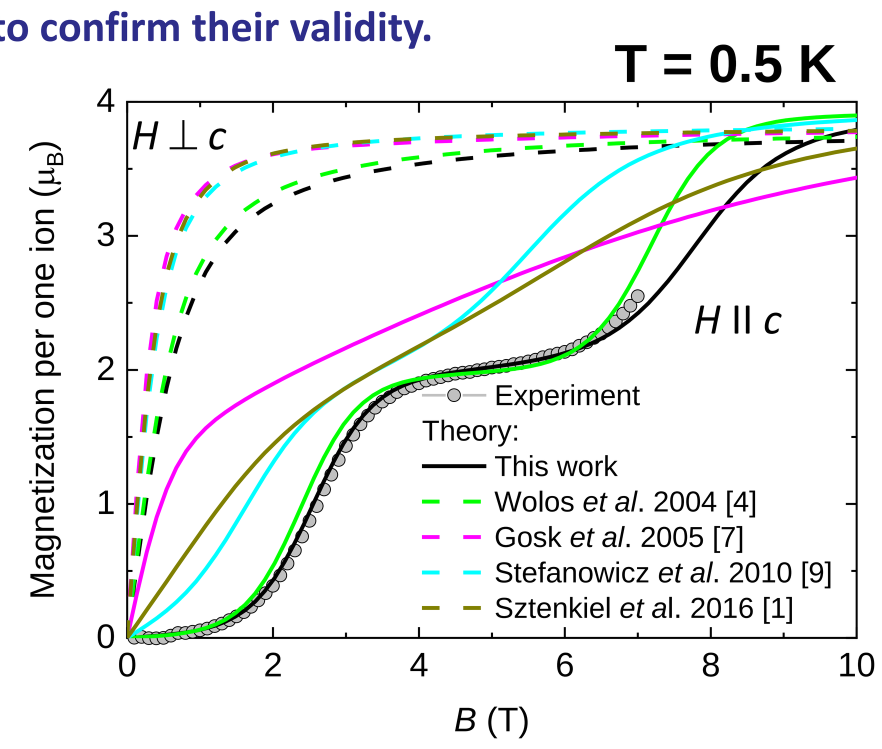
✓ $Mn^{3+}$ high spin configuration $^5T_2$ ($S = 2$, $L = 2$) [7,8]
confirmed by high-field EPR, EXAFS, XANES, XES
➔ Jahn-Teller effect
➔ single-ion uniaxial anisotropy in wurtzite structure



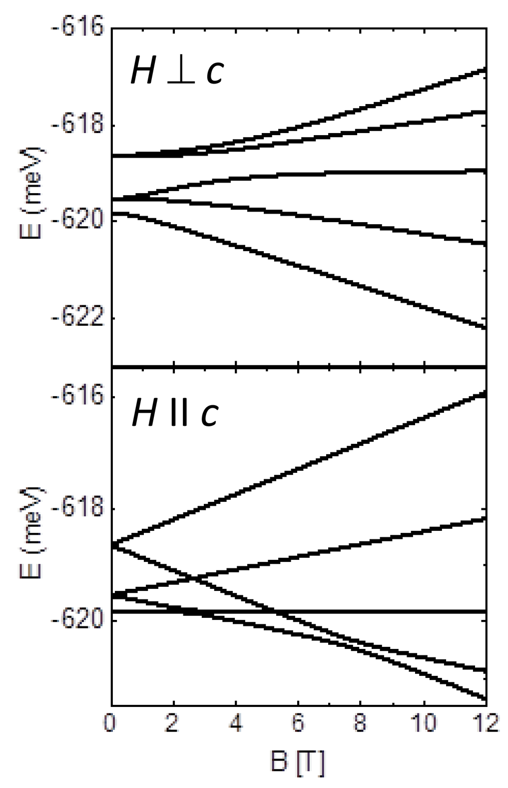




## Magnetization steps

**Very low temperature magnetometry (at $T = 0.5$ K) allows precise and fine adjustment of Hamiltonian* parameters. We use the same parameters at higher (liquid He temperatures) to confirm their validity.**




Magnetization of GaN:Mn crystal as a function of magnetic field parallel to *c*-axis (points). The solid and the dashed lines represent magnetization calculated for two orientations of magnetic field with the use of various parameters listed in the table below.

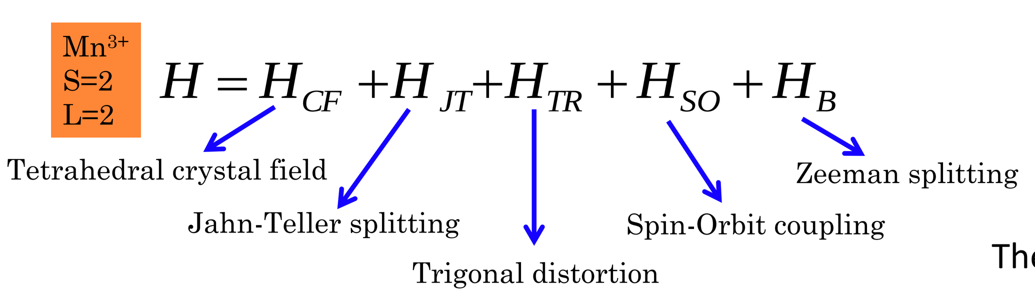



The energy of five lowest energy levels for Mn center in GaN calculated with the use of parameter set listed in the table below („this work").

| | $B_4$ | $B_2^0$ | $B_4^0$ | $\tilde{B}_2^0$ | $\tilde{B}_4^0$ | $\lambda_{TT}$ | $\lambda_{TE}$ |
|---|---|---|---|---|---|---|---|
| **This work, GaN:Mn crystals** | **11.44** | **4.03** | **0.0536** | **-5.25** | **-1.05** | **6.9** | **10.0** |
| Wolos *et al.* 2004 [4] GaN:Mn,Mg crystals | 11.44 | 4.00 | -0.560 | -5.25 | -1.05 | 6.5 | 10.0 |
| Gosk *et al.* 2005 [7] GaN:Mn,Mg crystals | 11.44 | 4.33 | -0.560 | -5.80 | -1.16 | 3.5 | 12.5 |
| Stefanowicz *et al.* 2010 [9] (Ga,Mn)N thin layers on $Al_2O_3$ | 11.44 | 4.20 | -0.560 | -5.10 | -1.02 | 5.0 | 10.0 |
| Sztenkiel *et al.* 2016 [1] (Ga,Mn)N thin layers on $Al_2O_3$ | 11.44 | 4.235 | -0.562 | 5.90 | -1.20 | 5.5 | 11.5 |

## *Hamiltonian

The energy structure of a single ion in $d^4$ configuration is described by Hamiltonian:




$$H = H_{CF} + H_{JT} + H_{TR} + H_{SO} + H_B$$

$$H_{CF} = -2/3 B_4 (\hat{O}_4^0 - 20\sqrt{2}\hat{O}_4^3)$$
$$H_{JT} = \tilde{B}_2^0 \hat{\Theta}_4^0 + \tilde{B}_4^0 \hat{\Theta}_4^2$$
$$H_{TR} = B_2^0 \hat{O}_4^0 + B_4^0 \hat{O}_4^2$$
$$H_{SO} = \lambda \hat{\boldsymbol{L}} \hat{\boldsymbol{S}}$$
$$H_B = \mu_B (g_L \hat{\boldsymbol{L}} + g_{Ls} \hat{\boldsymbol{S}}) \boldsymbol{B}$$

The (25x25) Hamiltonian matrix is parametrized by parameters: $B_i^k, \tilde{B}_i^k, \lambda_{TT}, \lambda_{TE}$

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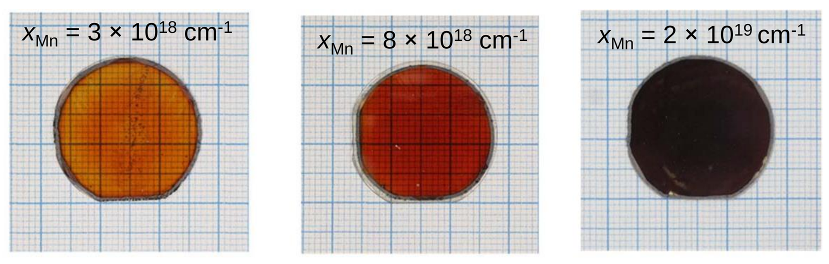
## Summary

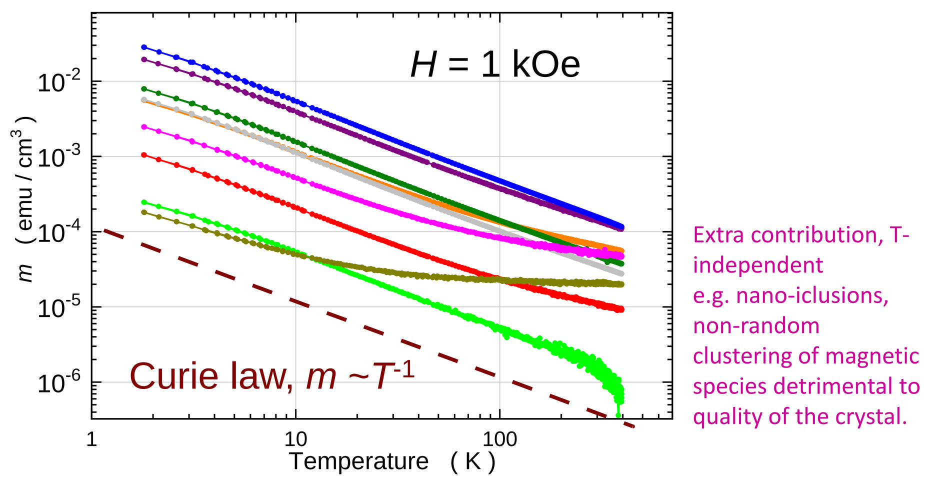
1. Unique and high quality GaN:Mn bulk crystals (1'' wafers) are investigated.
2. Magnetic measurements:
   a) Easily select out samples with non-random Mn-distribution (magnetically bound Mn) clusters.
   b) Provide measure on the abundance of $Mn^{3+}$ and $d^5$ ($Mn^{2+}$ and/or $Fe^{3+}$ species).
3. Further quantification of $Mn^{2+}$ and $Fe^{3+}$ content is based on room temperature EPR spectra.

To make point 2a operational we performed very-low-temperature magnetometry ($T = 0.5$ K) and $H$ up to 7 T to detect magnetization steps characteristic for $Mn^{3+}$ ion probed with $H \parallel c$. The complex form of the steps allows us to fine-tune the parameters needed to solve the Hamiltonian of $Mn^{3+}$ in GaN environment.

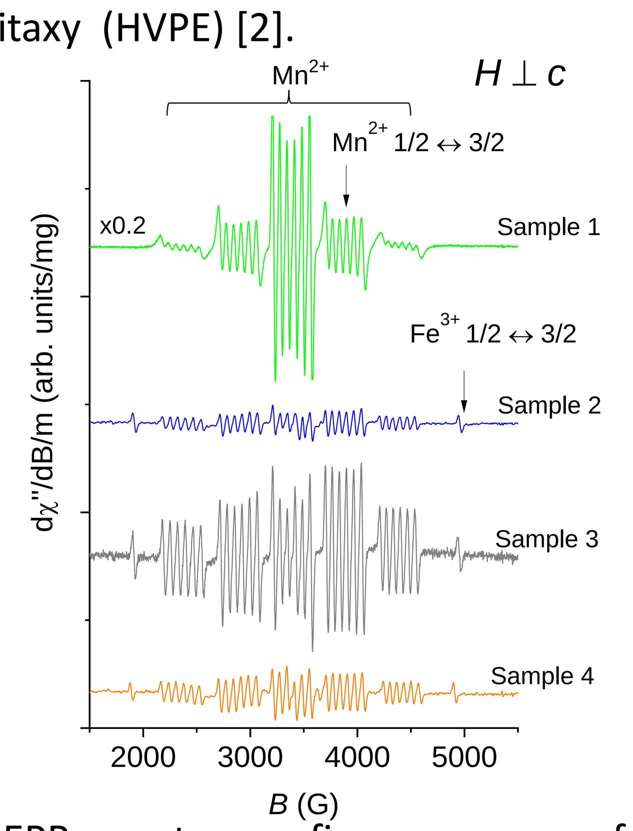
## Samples and basic characterization




Examples of GaN:Mn crystals grown by halide vapor phase epitaxy (HVPE) [2].



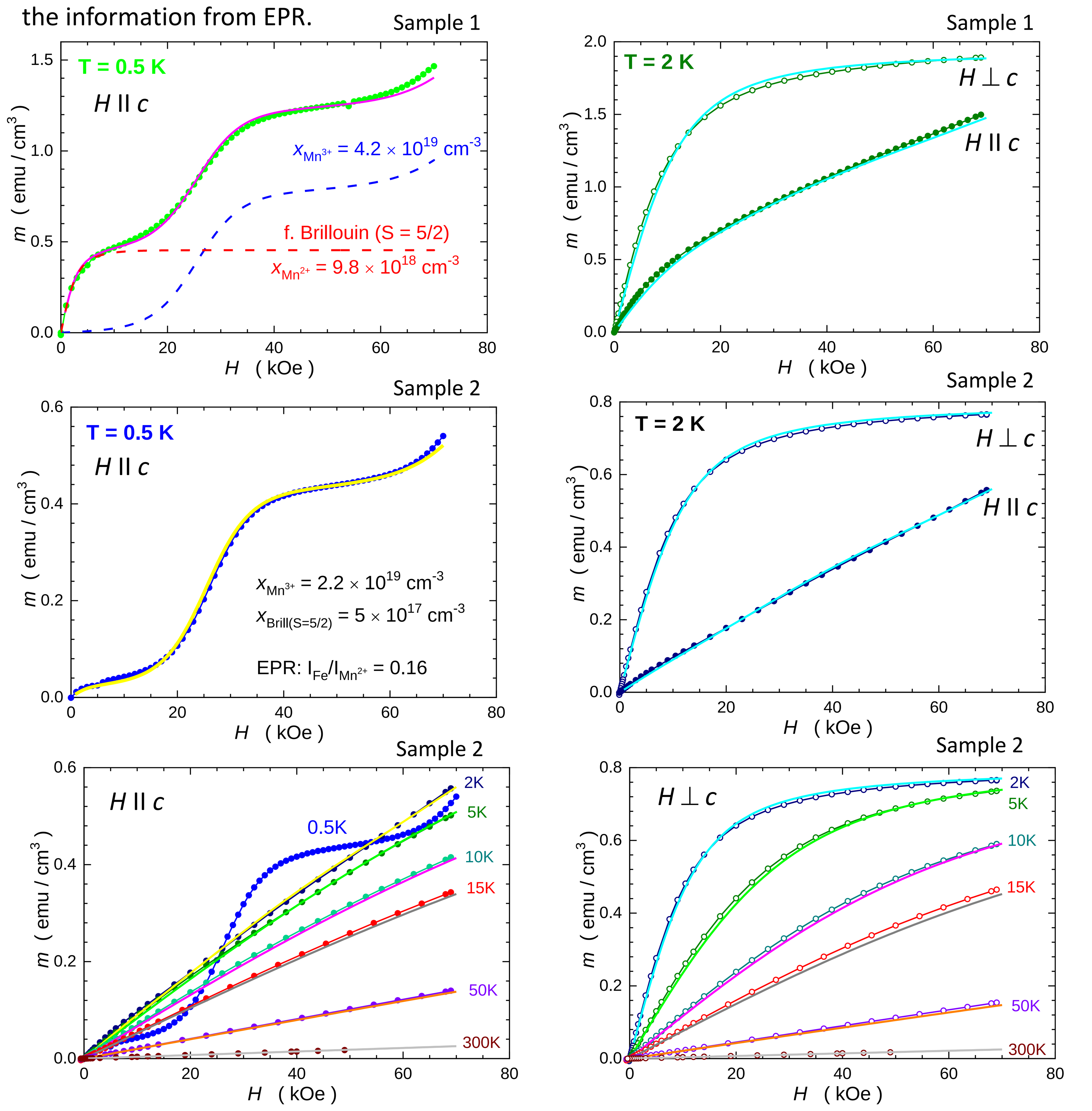

Basic $m(T)$ measurements discriminate between purely random (paramagnetic behavior) and inhomogeneous magnetic species distribution (seen as a leveling off at high temperatures- magenta and dark yellow)




EPR spectra confirm presence of additional $Mn^{2+}$ and $Fe^{3+}$ and quantify relative abundance of these two species.

## Modeling of magnetization

Detailed analysis of $m(H)$ gives quantitative information on $Mn^{3+}$ ($d^4$) and $d^5$ species ( $Mn^{2+}$ and $Fe^{3+}$) abundance. The absolute magnitudes of the two latter concentrations are obtained using the information from EPR.




Magnetization of GaN:Mn crystal as a function of magnetic field at selected temperatures. Parallel configuration – bullets, perpendicular to *c*-axis – open circles. The lines represent the modeled magnetization assuming two contributions. The first results from full Hamiltonian quantum calculations for $Mn^{3+}$ in GaN, the second is the isotropic Brillouin function for S = 5/2.

## References

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