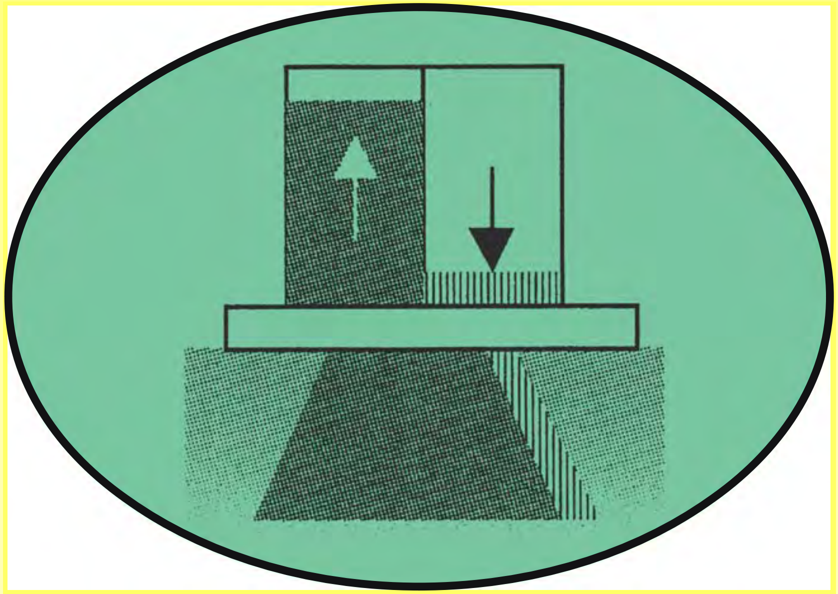
Ferromagnetic Semiconductors with high Curie Temperature and Unusual Magnetic Properties

The case of Gd-doped GaN



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Outline

1. Motivation and previous work
2. Growth of Gd-doped GaN
    - Growth conditions and Gd - incorporation
    - Structural properties
3. Magnetic properties of Gd-doped GaN
    - Magnetic hysteresis and FC and ZFC measurements
    - Colossal magnetic moment per Gd atom
    - XLD and XMCD measurements
    - Magneto-photoluminescence
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    - Empirical model
    - Magnetic phases and anisotropy
    - Influence of defects on ferromagnetism
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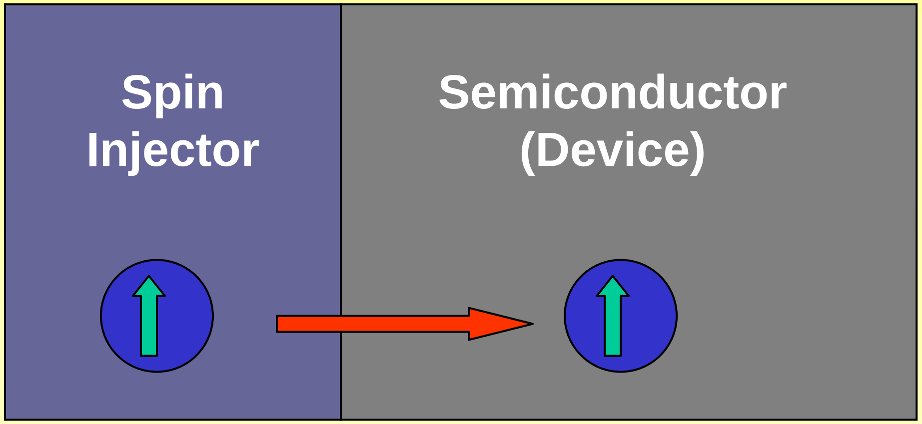
Materials for spin injection

Spintronics

Generation, conservation, manipulation of coherence of electronic states and of their magnetic spin properties

Electrical injection of polarized carrieres



Ferromagnetic semiconductor, metal or half-metal?

Magnetic semiconductors

Europium Chalcogenides
(EuO, EuS, EuSe)

S. Von Molnar, S. Methfessel „Giant negativef magnetoresistance in ferromagnetic Eu1-xGdxSe“
J. Appl. Phys. 38 (1967) 959

L. Esaki, P. Stiles S. von Molnar „Magneto internal field emission in junction of magnetic insulators“
Phys. Rev. Lett. 19 (1967) 852

P. Kasuya and A. Yanase „Anomalous transport phenomena in Eu-chalcogenide alloys“
Rev. Mod. Phys. 40 (1968) 684

E. L. Nagaev „Physics of Magnetic Semiconductors“ (Mir, Moscow, 1983)

II-VI compounds alloyed with Mn(Cr)
[(Cd,Mn)Te, (Zn,Mn)Se]

J. K. Furdyna and J. Kossut (Eds.) Semiconductors and Semimetals, Vol. 25 (Academic Press, New York, 1988)

IV-VI compounds alloyed with Mn
[(Pb,Sn,Mn)Se]

T. Story, H. H. Galazka, R. B. Frankel, and P. A. Wolf, Phys. Rev. Lett. 56 (1986) 777

Advantages of wide-gap semiconductors

Theoretical models

Dietl et al. [Science 287(2000)1019] proposed a Zener-like exchange mediated by itinerant holes. The transition-metal (TM) ions provide a local spin, and the delocalized holes mediate a RKKY-like interaction between the localized TM moments resulting in ferromagnetic behavior.

Based on this model, high Curie temperatures were predicted for Mn- doped wide-gap semiconductors with high hole concentrations.

However: Experimental results obtained by different groups from TM-doped wide-gap semiconductors are controversely discussed and often not reproducible

In general the actual exchange mechnism in ferromagnetic semiconductors is still a matter of controversy.

Magnetic semiconducting oxides

K. Nielsen, S. Bauer, M. Lübbe, S.T.B. Goennenwein, M. Opel et al.

"Ferromagnetism in epitaxial (Zn,Co)O films grown on ZnO and Al_2O_3"
Phys. Status Solidi A203 (2006) 3581

T. Fukumura, H. Toyosaki, and Y. Yamada

„Magnetic oxide semiconductors“
Semicond. Sci. Technol. 20 (2005) S103

S. J. Pearton, W. H. Heo, M. Ivill, D. P. Norton and T. Steiner

„Dilute magnetic semiconducting oxides“
Semicond. Sci. Technol. 18 (2004) R59

S. A. Chambers and R. F. C. Farrow

„New possibilities for ferromagnetic semiconductors“
MRS Bulletin 28 (10) (2003) 729

Advantage of III-Nitrides

Theoretical models:

In addition to the proposal of Dietl et al., the first-principle calculations of Katayama-Yoshida et al. [Semicond. Sci. Technol. 17 (2000) 377] have indicated that TM-doping of GaN should lead to ferromagnetic material.

Experiments:

Numerous attempts were made to synthesize single-phase GaN alloyed with Mn, Cr, Fe, Co, V.......

For a review see: A. Bonanni, Semicond. Sci. Technol. 22 (2007) R41

The experimental results obtained by different groups from TM-doped GaN are a matter of controversy (insulating material, precipitation, phase separation, spinoidal decomposition).

Rare-earth (RE) doping of GaN

- Sharp RE intra-f-shell optical transitions allow light emission in the visible to infrared spectral range
  - Eu-doped GaN $\rightarrow$ 623 nm emission
  - Er-doped GaN $\rightarrow$ 1.55 µm emission

- Isovalent RE^{3+} ions on Ga lattice sites form electrically inert centers (no deep gap states)

Ref: P. N. Favennec et al., Electron Lett. 25 (1989) 718
Y. Q. Wang and A. J. Steckl, Appl. Phys. Lett. 82 (2003) 402
J. S. Filhol et al., Appl. Phys. Lett. 84 (2004) 2841

- Magnetic coupling of partially filled 4f-orbitals of RE^{3+} ions possibly weaker than d-orbitals in transition metals

- Gd has both partially filled 4f and 5d orbitals
  $\rightarrow$ new coupling mechanism?

Ref: M. Hashimoto et al., Jpn. J. Appl. Phys. 42 (2003) L1112
N. Teraguchi et al., Solid State Commun. 122 (2002) 651

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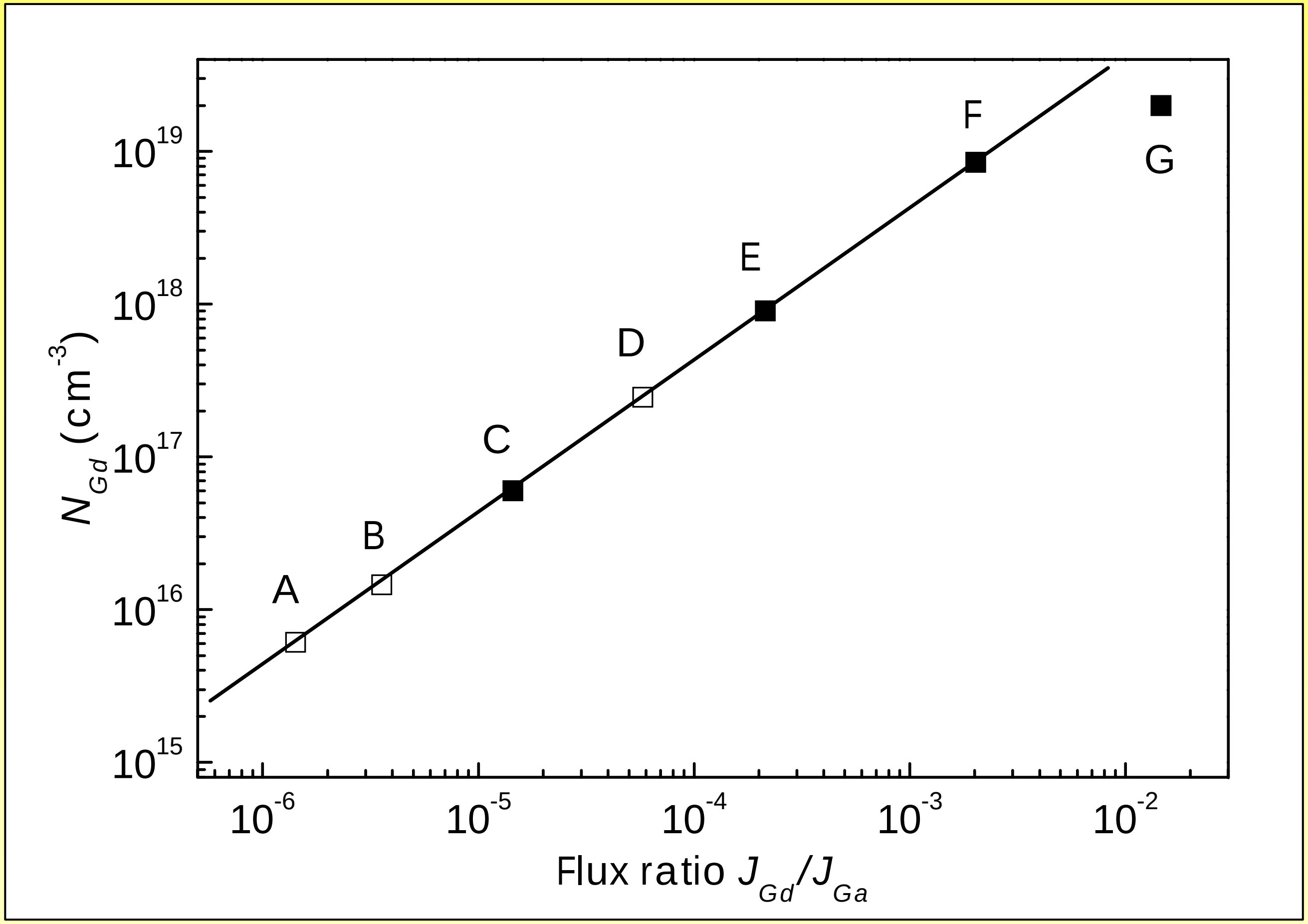
Growth of Gd-doped GaN

- Reactive (NH_3) molecular beam epitaxy (R-MBE)
- 4N (99,00%) Gd ingots from Stanford Mater. Corp.,
- T_e = 950 - 1300° C ($\rightarrow$below melting point of Gd)
- 6H-SiC(0001) substrates, T_s = 810° C, no buffer layer
- Growth rate = 0.6µm/hr
- (2 x 2) surface reconstruction
- Atomically flat surface with monolayer steps
- Unity sticking coefficient of Gd on GaN(0001) up to 10^{19} cm^{-3}

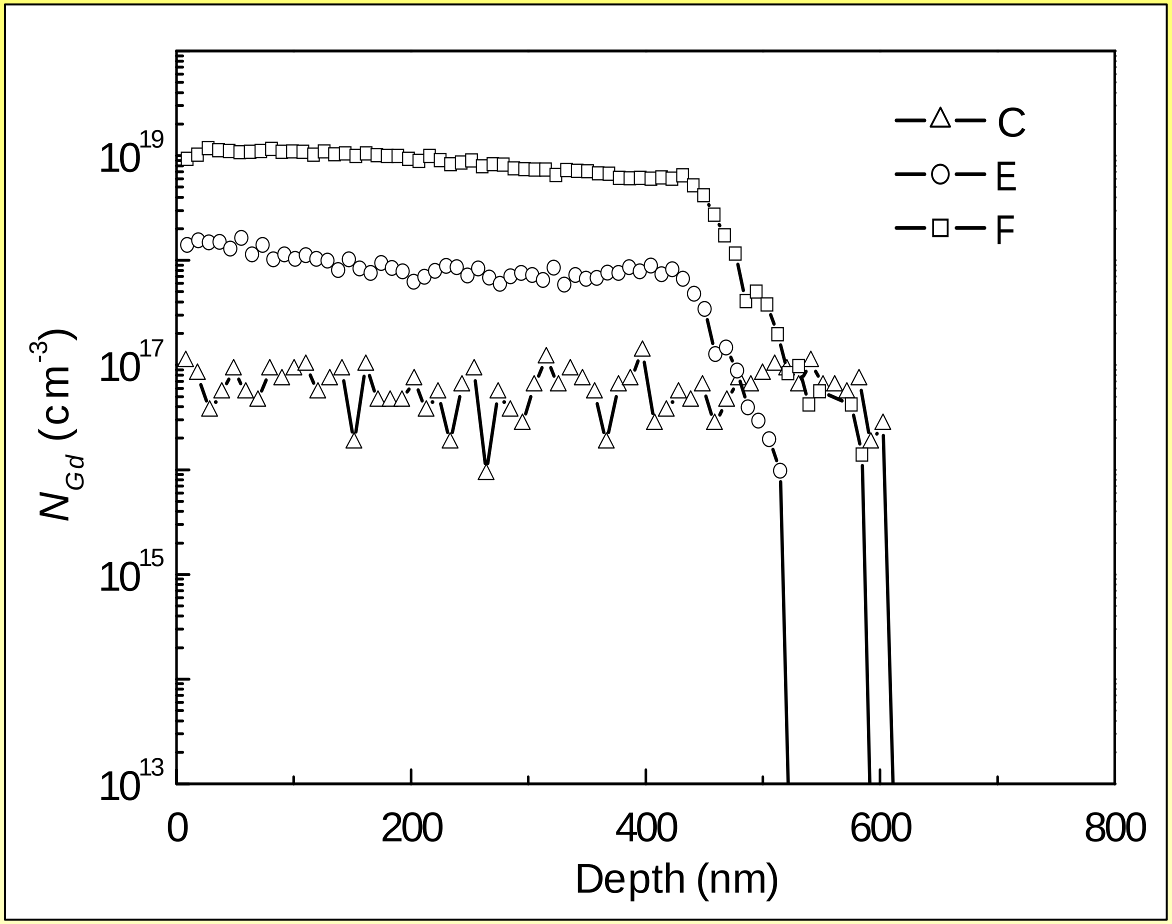
→ **Gd-doped GaN layers are insulating ("dilute magnetic dielectric")**

Gd concentration vs Gd/Ga flux ratio



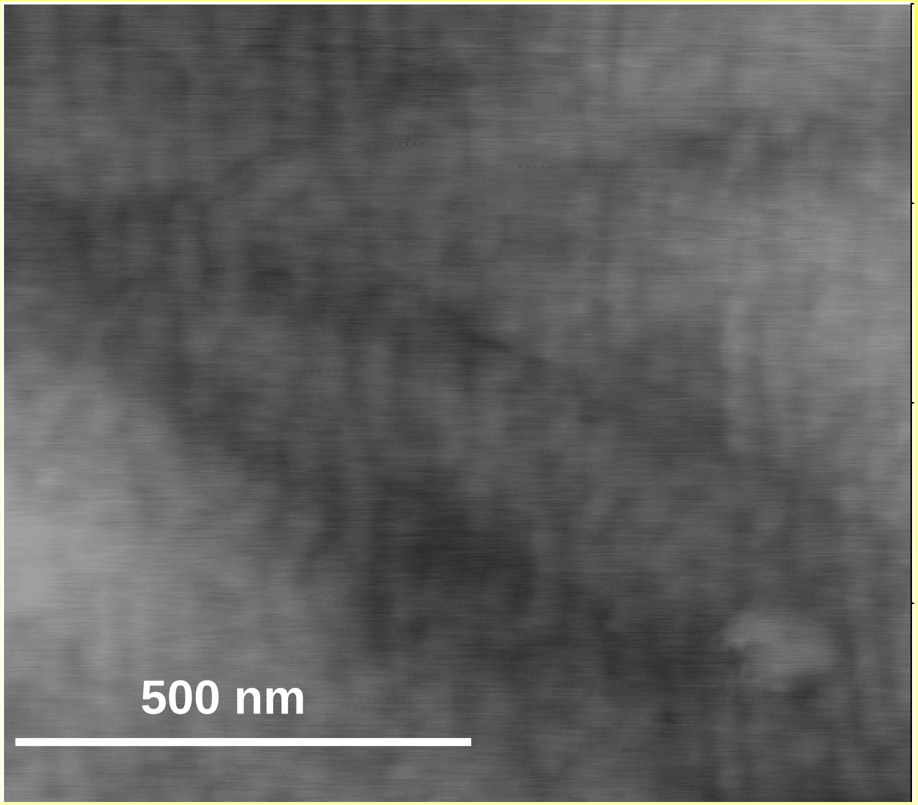
Unity sticking coefficient of Gd up to 10^{19} cm^{-3}

SIMS depth profiles of Gd-doped GaN layers



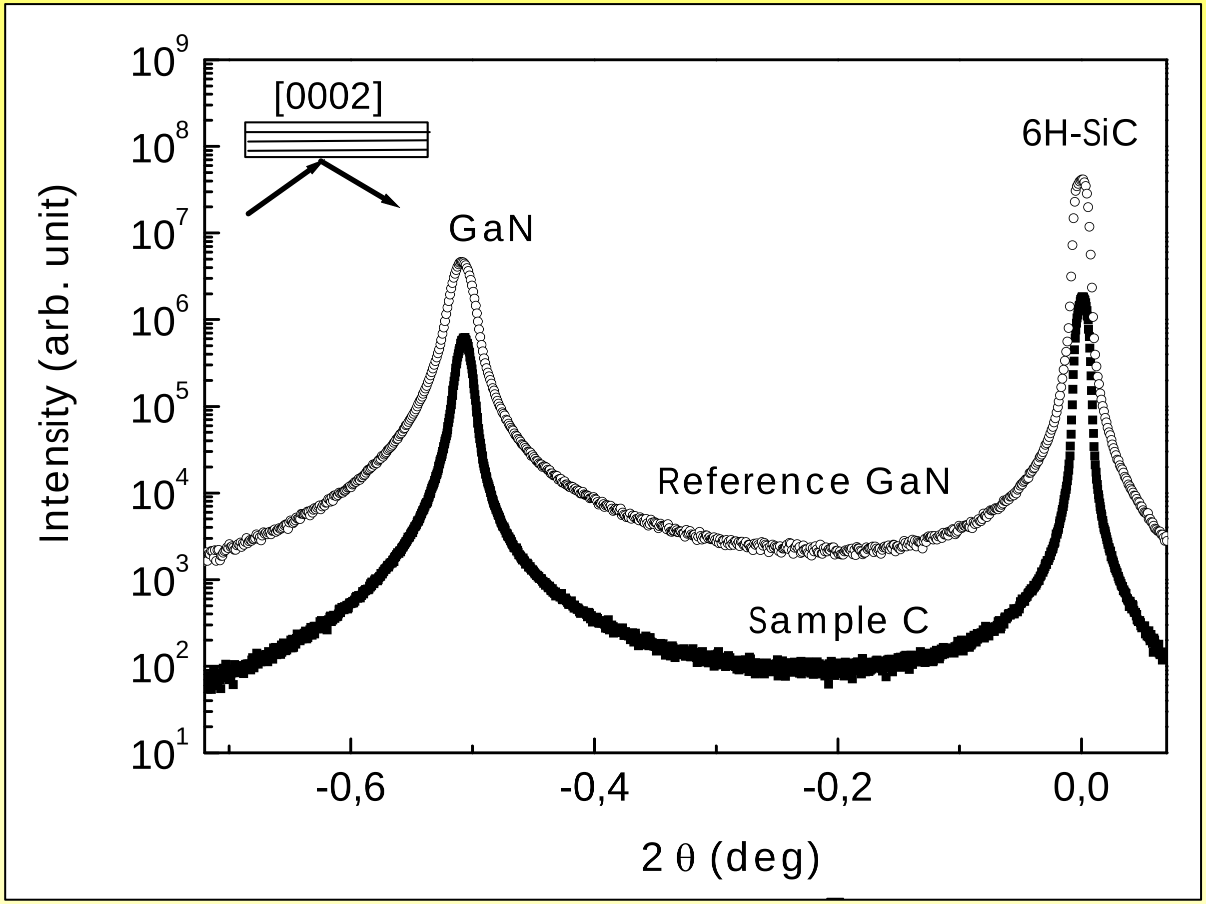
Flat Gd doping profiles

AFM surface image of GaN:Gd ($1x10^{19}$ cm^{-3})



rms roughness: 0.14 nm
ptv roughness: 3 nm
} 1 µm x 1 µm scan

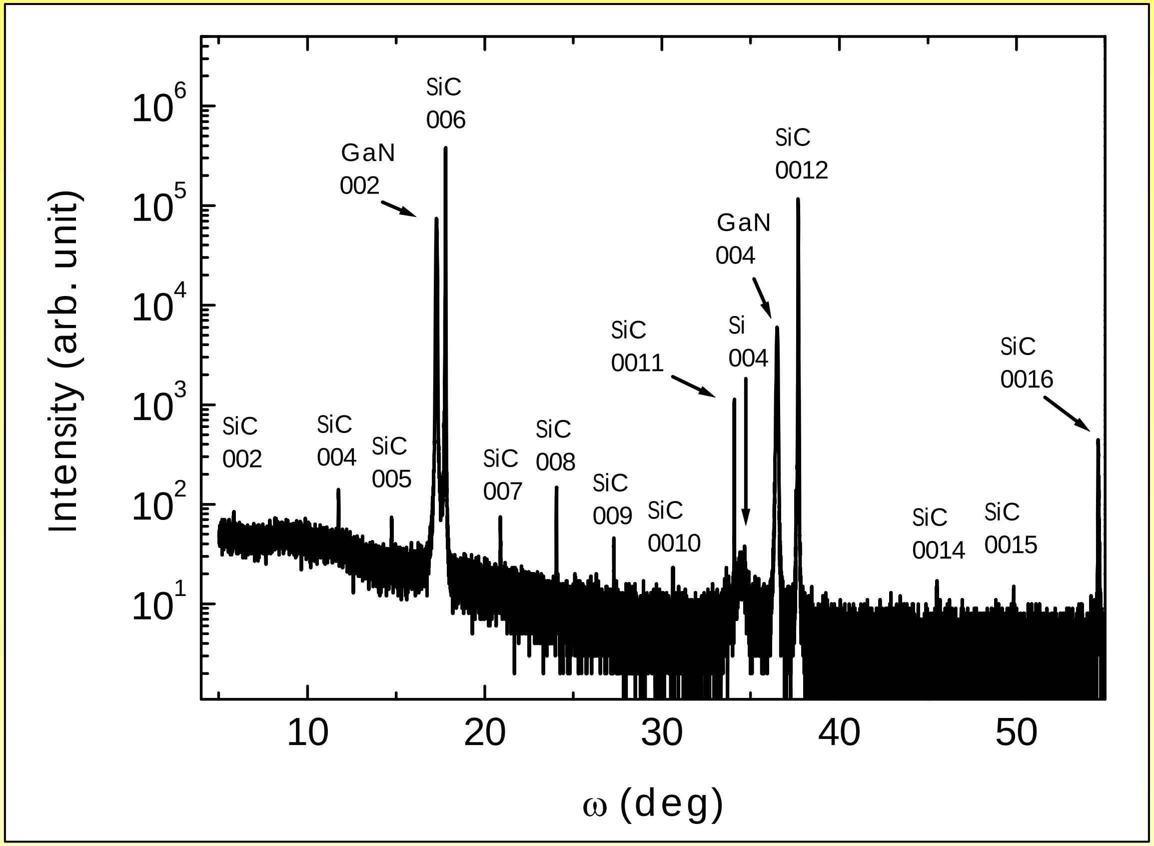
X-ray diffraction (ω – 2 θ scan)



300“ width for symmetric (0002) reflection

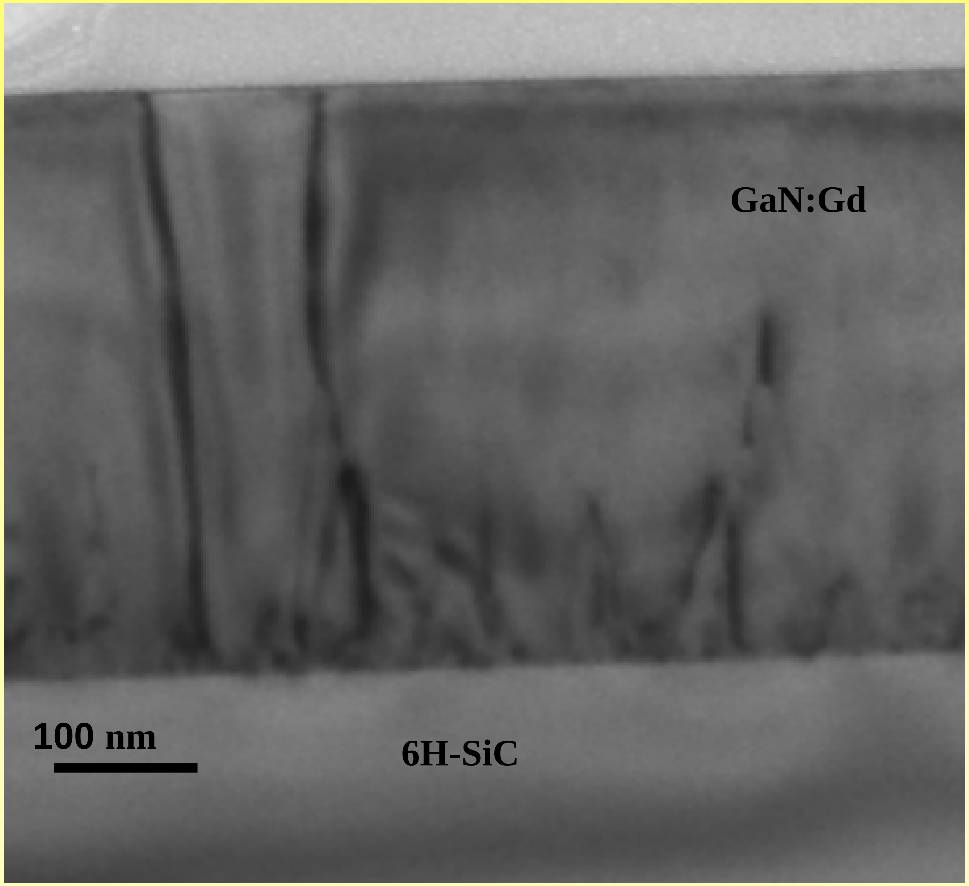
900“ width for asymmetric (1105) reflection

X-ray diffraction (ω – 2 θ)



No secondary phase detected

Bright–field cross-sectional TEM



Dark lines arise from screw dislocations

Contrast at interface due to dislocation loops

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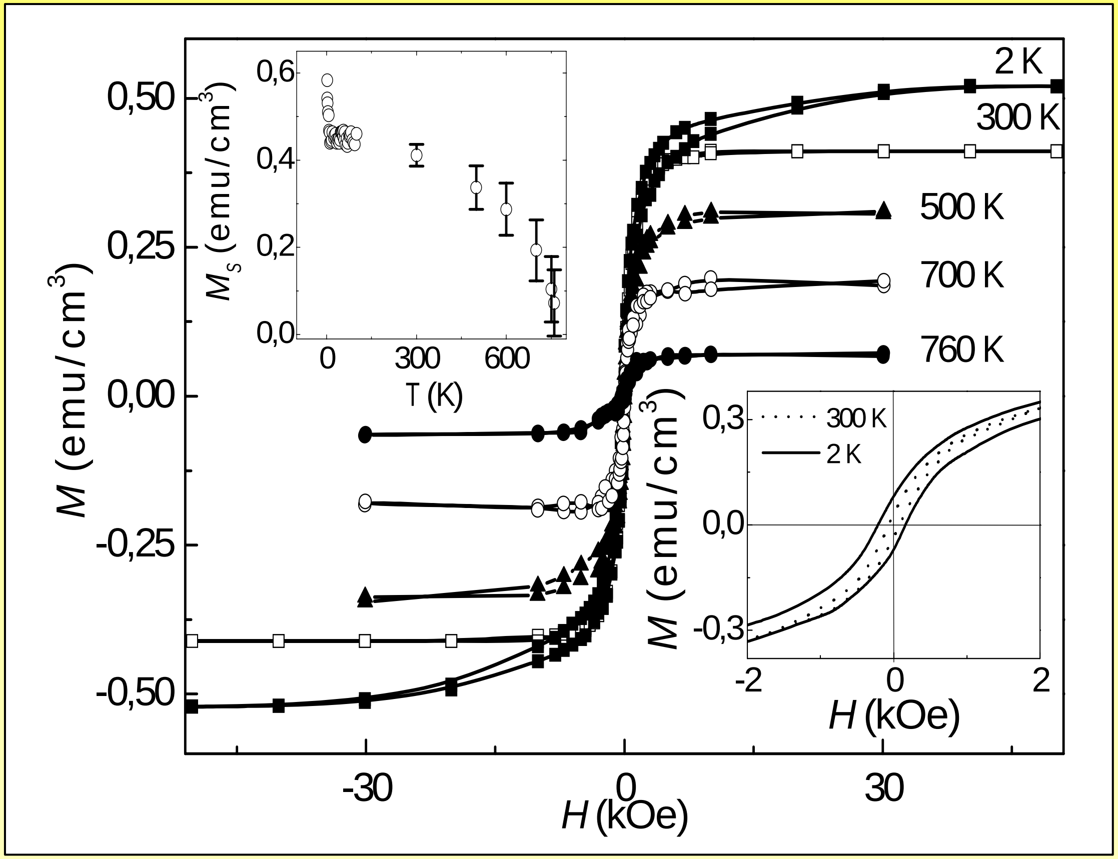
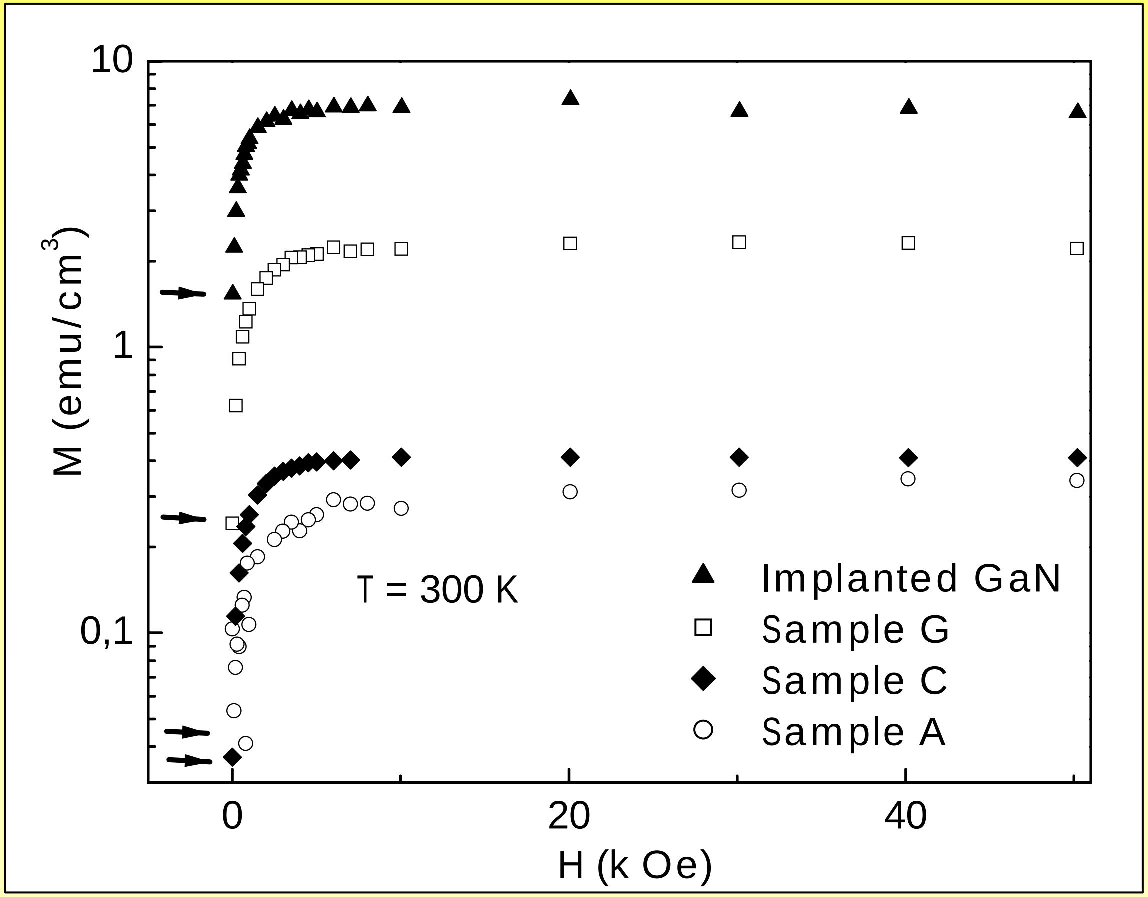
Magnetic hysteresis ([Gd] = 6 x 10^{16} cm^{-3})



Magnetization saturates at high fields $\Rightarrow$ Ferromagnetism

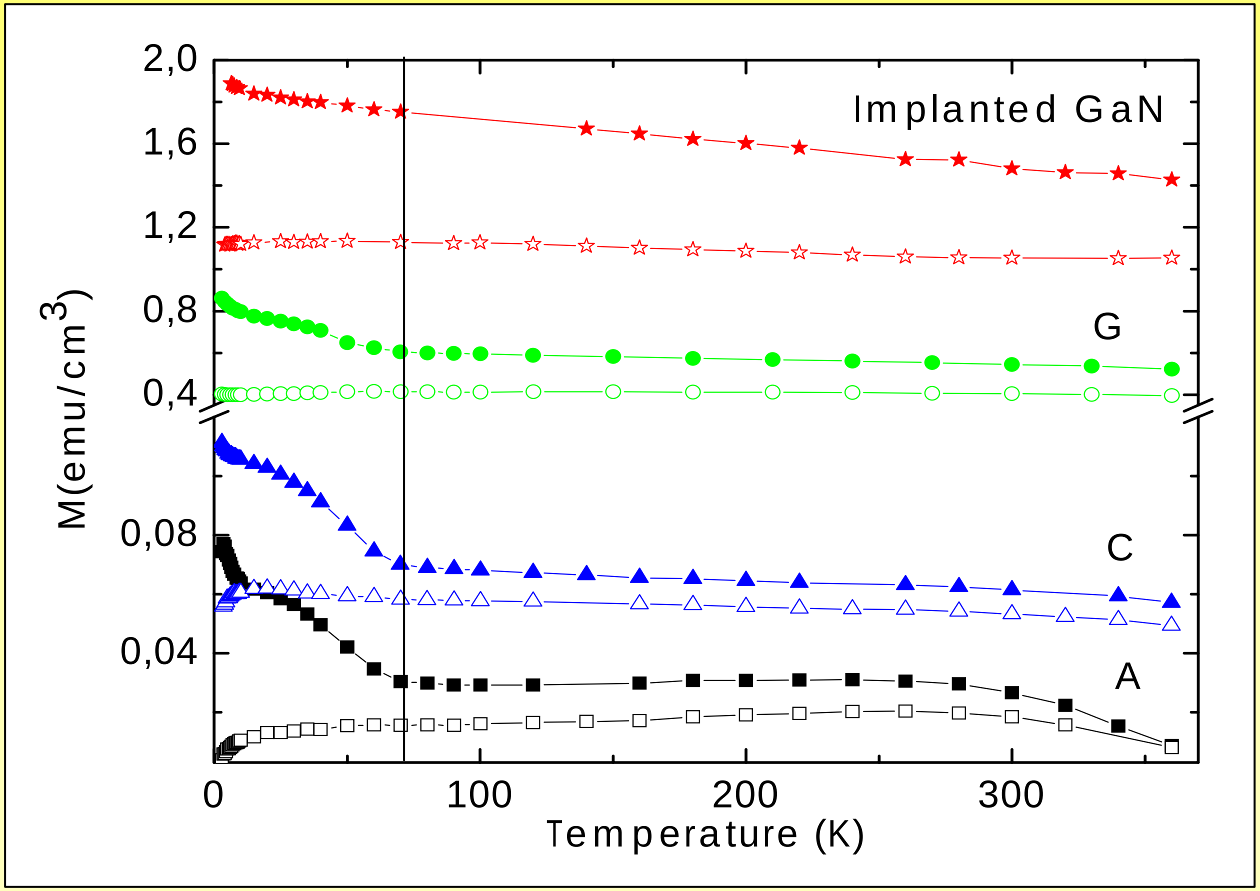
Superposition of two loops with different H_c and M_r at 2 K ?
$\rightarrow$ above 10 K phase with larger H_c and M_r disappears

Details of hysteresis curves



Arrows indicate value of M_r

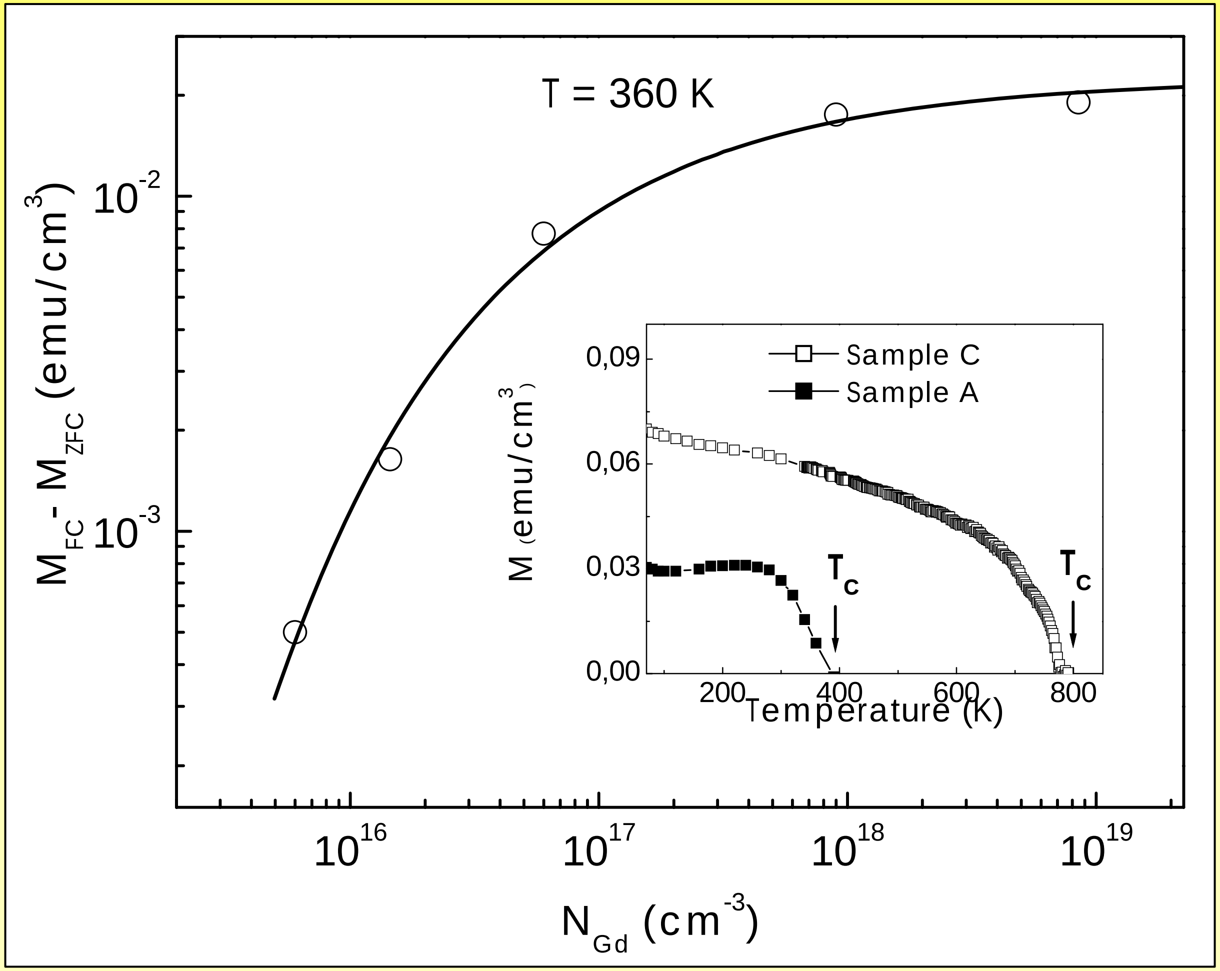
T dependence of FC and ZFC magnetization



Double-step structure in FC curve below 70 K

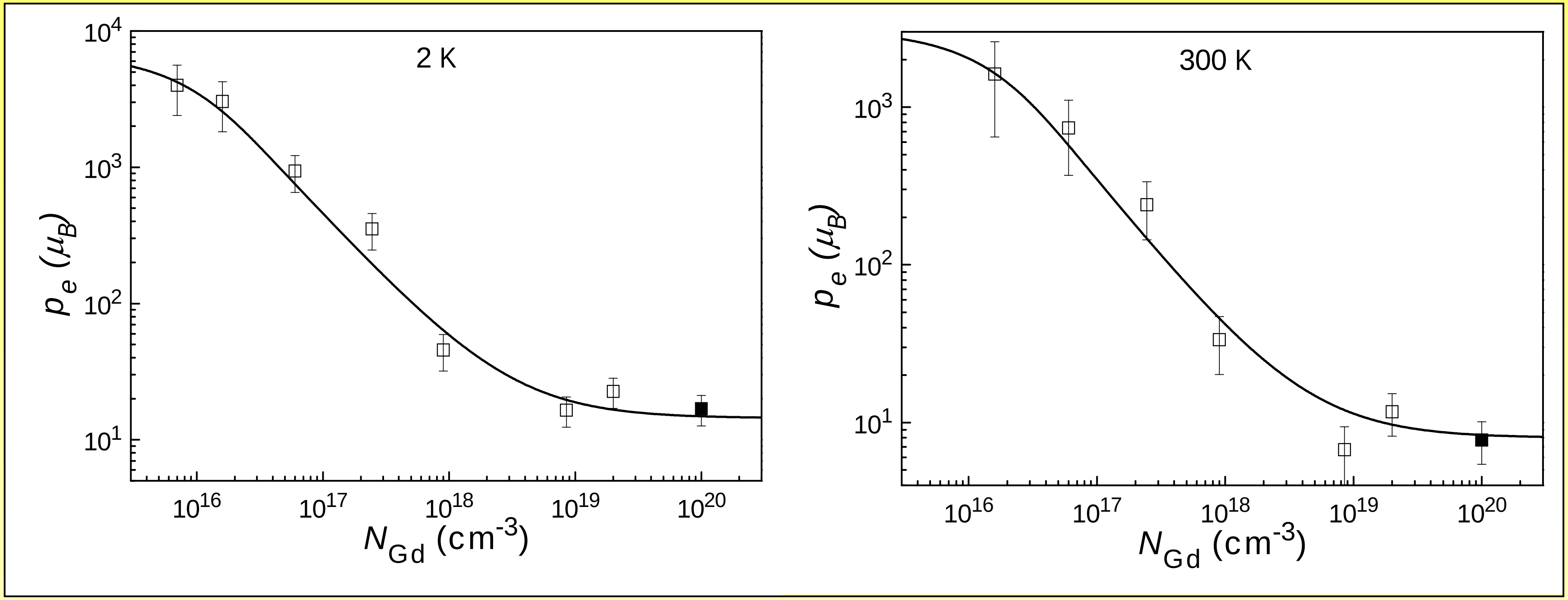
Step at 10 K indicates phase with larger H_c and M_r

Difference between FC and ZFC magnetization



Inset: Magnetization vs T at 100 Oe

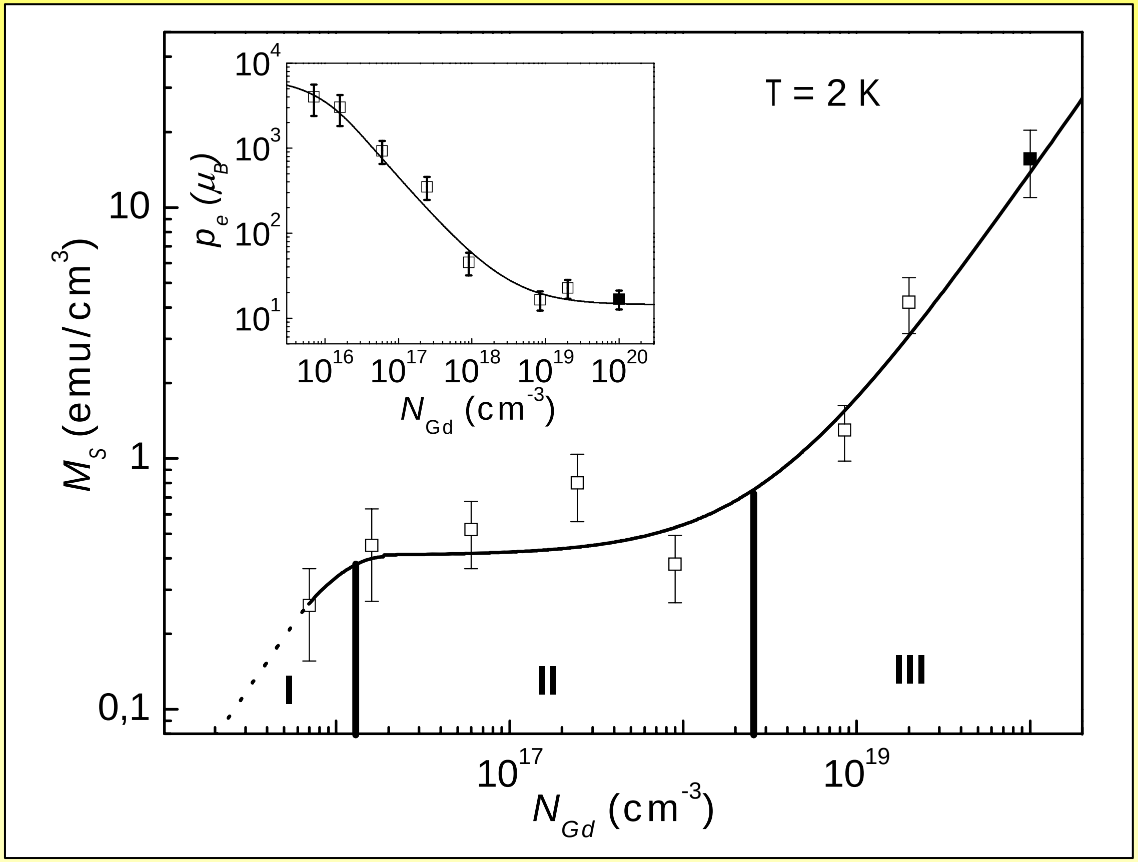
Average magnetic moment per Gd atom



Average moment at 2 K per Gd atom is as high as **4000 μ_B**

Values are obtained from the measured magnetization and the measured concentration

Saturation magnetization vs [Gd]

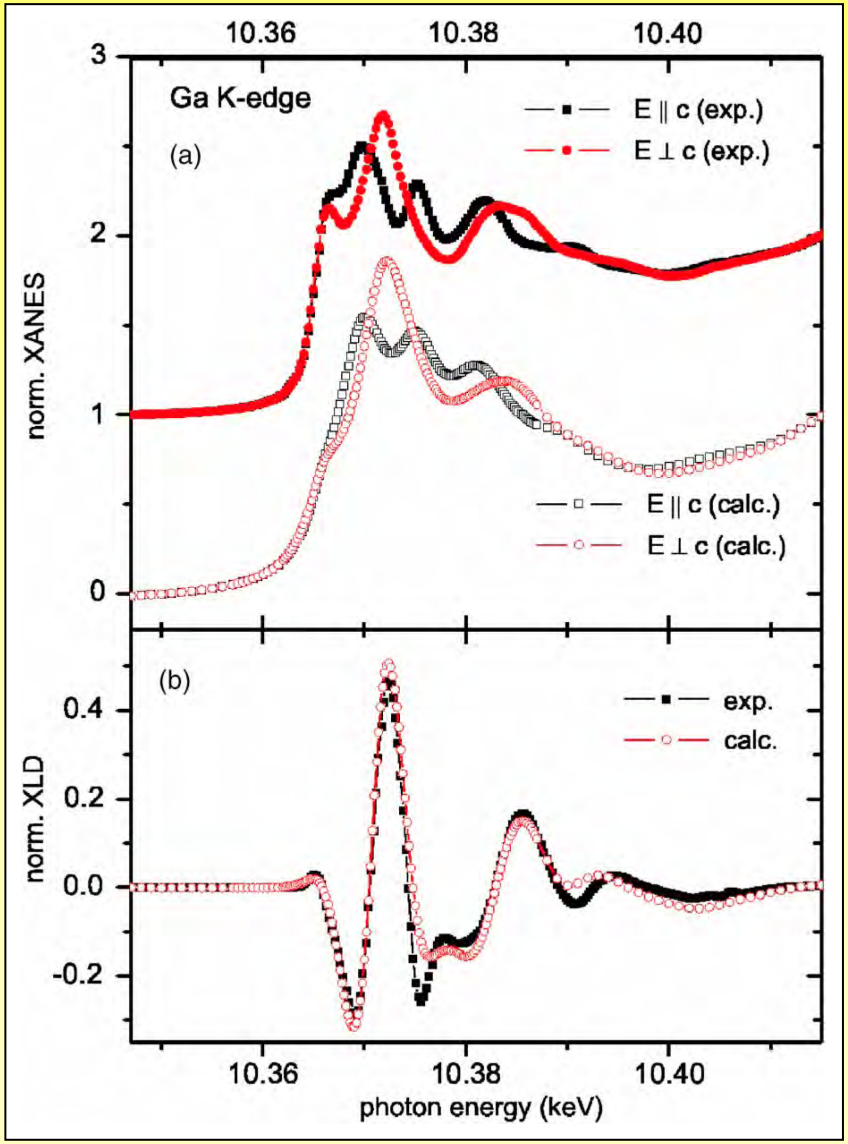


Regime I : M_s increases with [*Gd*] up to percolation threshold

Regime II: M_s is independent of [*Gd*] and ρ_{eff} decreases with [*Gd*]

Regime III: M_s increases again with [*Gd*] and ρ_{eff} approaches saturation

XANES and XLD measurements from Gd-doped GaN

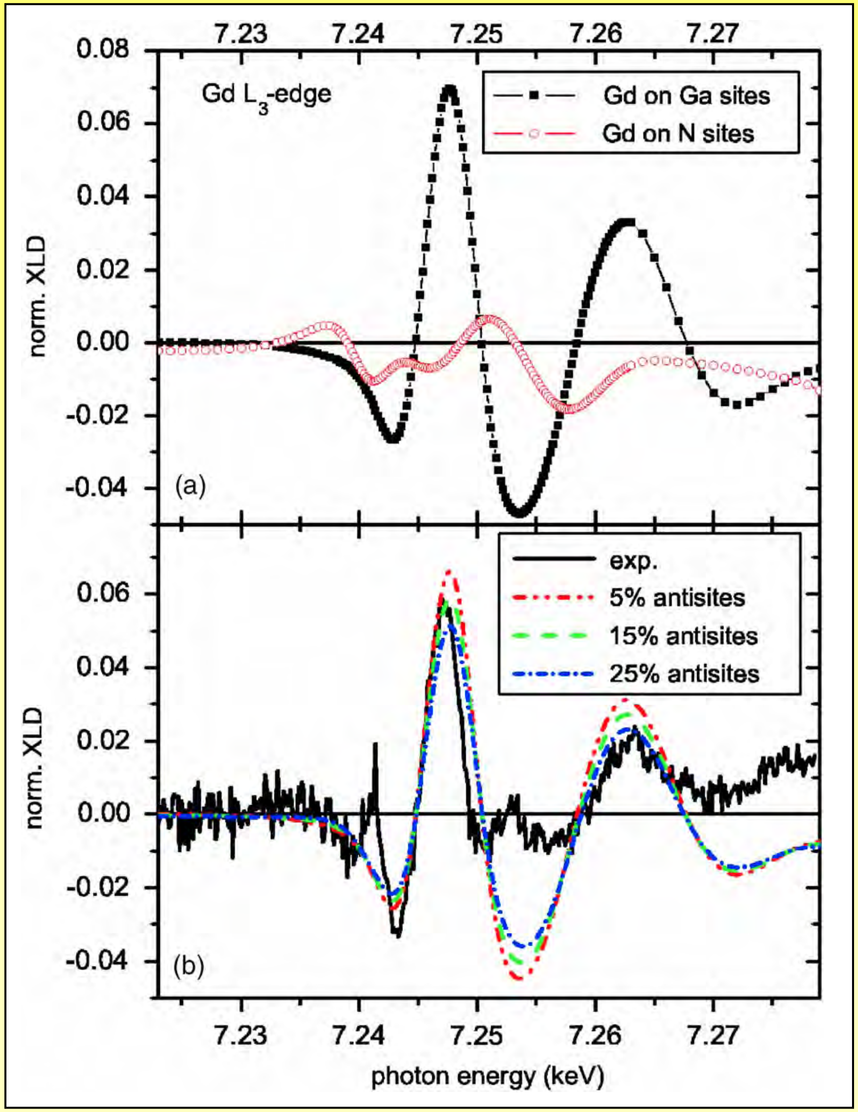


Probing of Gd L_3 edge in addition to Ga K edge is only possible for high Gd concentrations

XANES = X-ray absorption near edge spectra

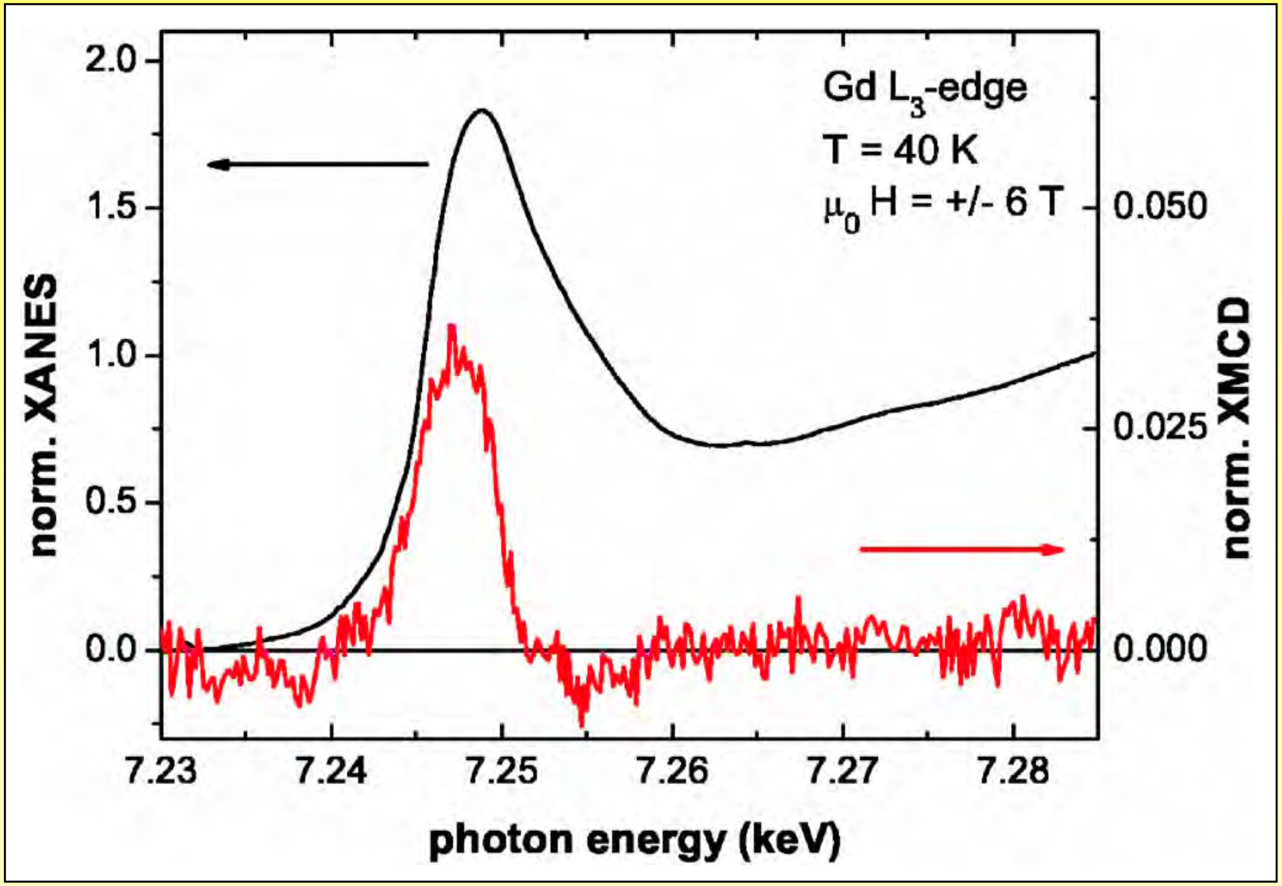
XLD = X-ray linear dichroism

XLD spectra at Gd L_3 edge



Comparison of measurements with simulations for Gd on Ga sites and on N sites (antisites)

Normalized XANES and XMCD spectra of GaN:Gd

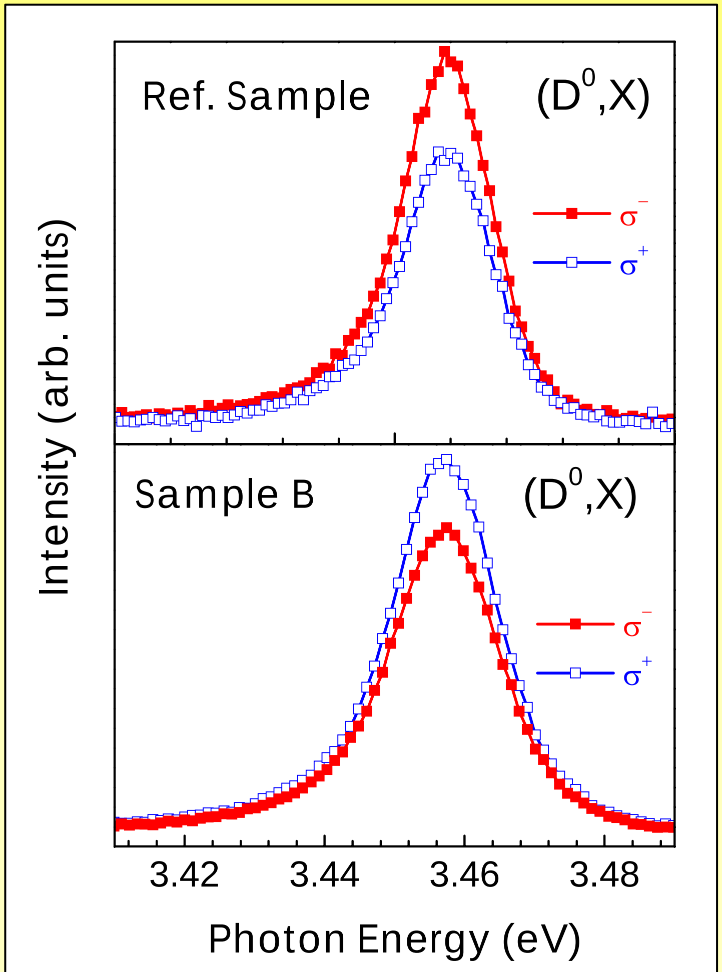


Difference spectra were taken in magnetic field of 6 T

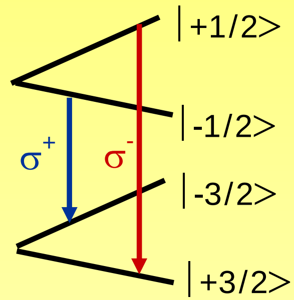
Magneto-photoluminescence

PL spectra of all samples dominated by (D^{o},X) transition due to O donors

B = 10 T in Faraday geometry (**B || c**)

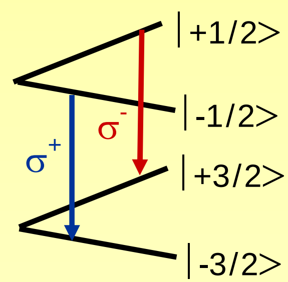


⇔



Polarization of sample B has opposite sign as compared to the reference sample

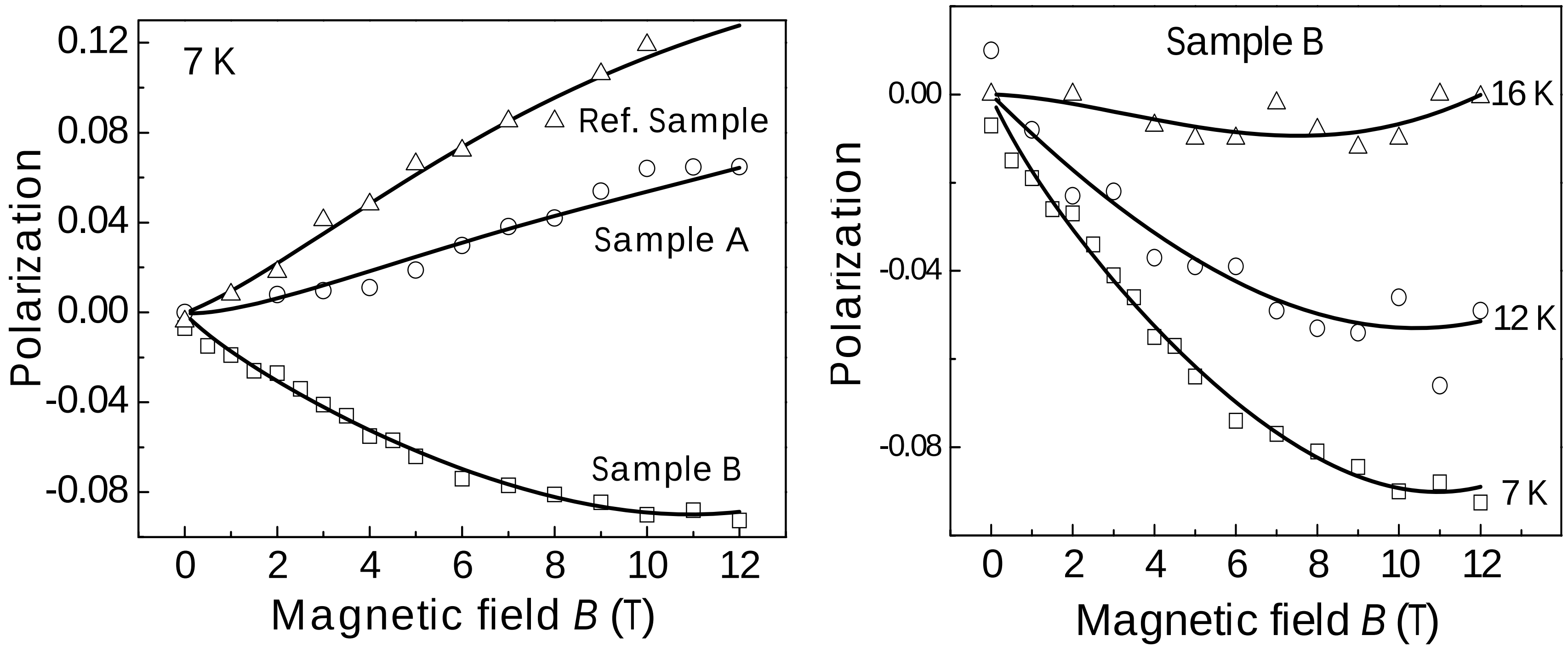
⇔



Average Gd to (D^{o},X) distance ≈ 12 nm

⇒ Gd has a long-range influence on the GaN matrix

Temperature and field dependence of PL polarization



Polarization $\rho = (I^{\sigma^-} - I^{\sigma^+}) / (I^{\sigma^-} + I^{\sigma^+})$

Relative change of the polarization increases with N_{Gd}

Polarization becomes negligible only above 16 K (=1.4 meV)

$\Rightarrow$ Gd-induced energy splitting $>$ 1.4 meV

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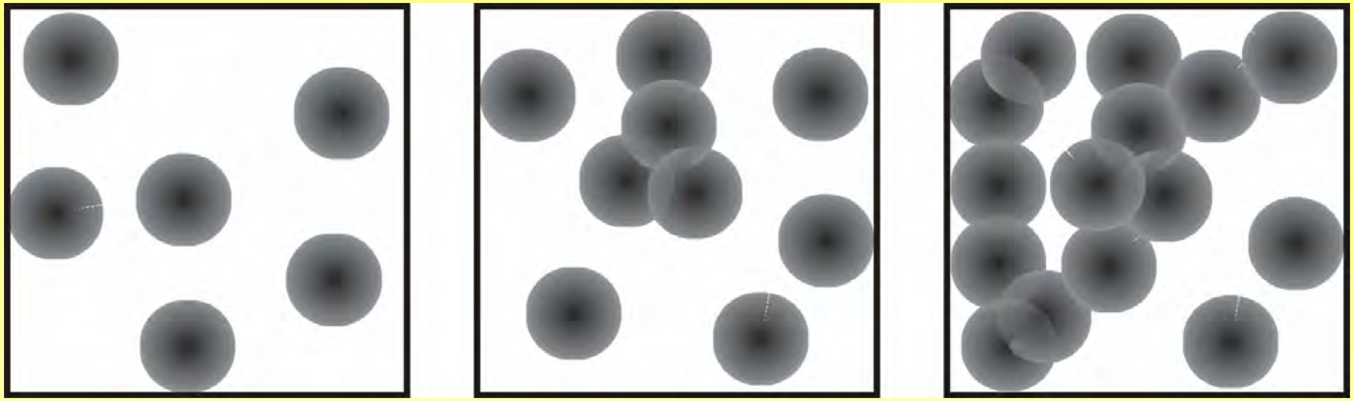
Empirical model for origins of colossal moment

Gd atoms polarize the matrix



$p_e = p_{Gd} + p_m \nu N_o/N_{Gd}$; $\nu = 1\text{-}\exp(-v N_{Gd})$

p_e decreases as N_{Gd} is increased $\rightarrow$ experimentally observed

Overlap of spheres $\rightarrow$ ferromagnetic coupling

T_c increases with N_{Gd} $\rightarrow$ experimentally observed

Details of empirical model

Saturation magnetization

$$M_s = p_{Gd} N_{Gd} + p_0 \tilde{v} N_0 + p_1 N_0 \sum_{n=2}^{N_{Gd}} n \tilde{v}_n$$

N_0 = concentration of matrix atoms per unit volume

ν = volume of each sphere

$$\tilde{v}_n = \frac{(vN_{Gd})^n}{n!} e^{-vN_{Gd}} =$$

Volume fraction of the regions contained within *n* spheres

Average effective magnetic moment per Gd atom

$$p_{eff} = p_{Gd} + p_1 N_0 v + [p_0 - (p_{0+} p_1 N_{Gd} v) e^{-vN_{Gd}}] \frac{N_0}{N_{Gd}}$$

Fit of experimental M_s vs N_{Gd} data

$p_{Gd} = 8\ \mu_B$

Fit parameter	2 K	300 K
	$p_0 = 1.1 \times 10^{-3}\ \mu_B$	$8.4 \times 10^{-4}\ \mu_B$
	$p_1 = 1.0 \times 10^{-5}\ \mu_B$	≈ 0
	r = 33 nm	28 nm

Three regimes in M_s vs N_{Gd} curve:

I. Spheres are separated and p_{eff} has maximum value

$\rightarrow$ M_s increases with N_{Gd} as $\tilde{\nu}$ grows with N_{Gd}

II. N_{Gd} has crossed percolation threshold and $p_1 \approx 0$

$\rightarrow$ M_s independent on N_{Gd}

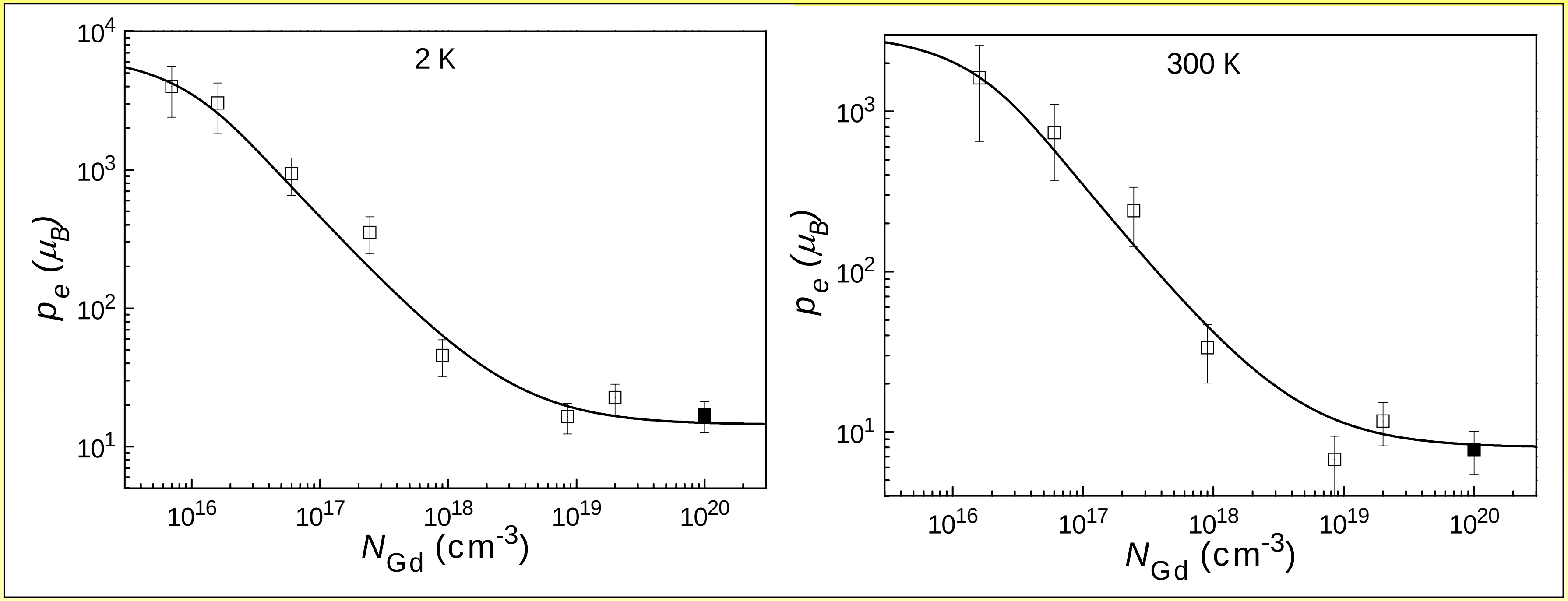
$\rightarrow$ p_{eff} decreases with N_{Gd}

III. Entire GaN matrix is polarized

$\rightarrow$ First term of equation dominates, i.e. M_s increases with N_{Gd}

$\rightarrow$ p_{eff} starts to saturate (value by amount of $p_1 N_0 v$ larger than 8 μB)

Colossal Magnetic Moments



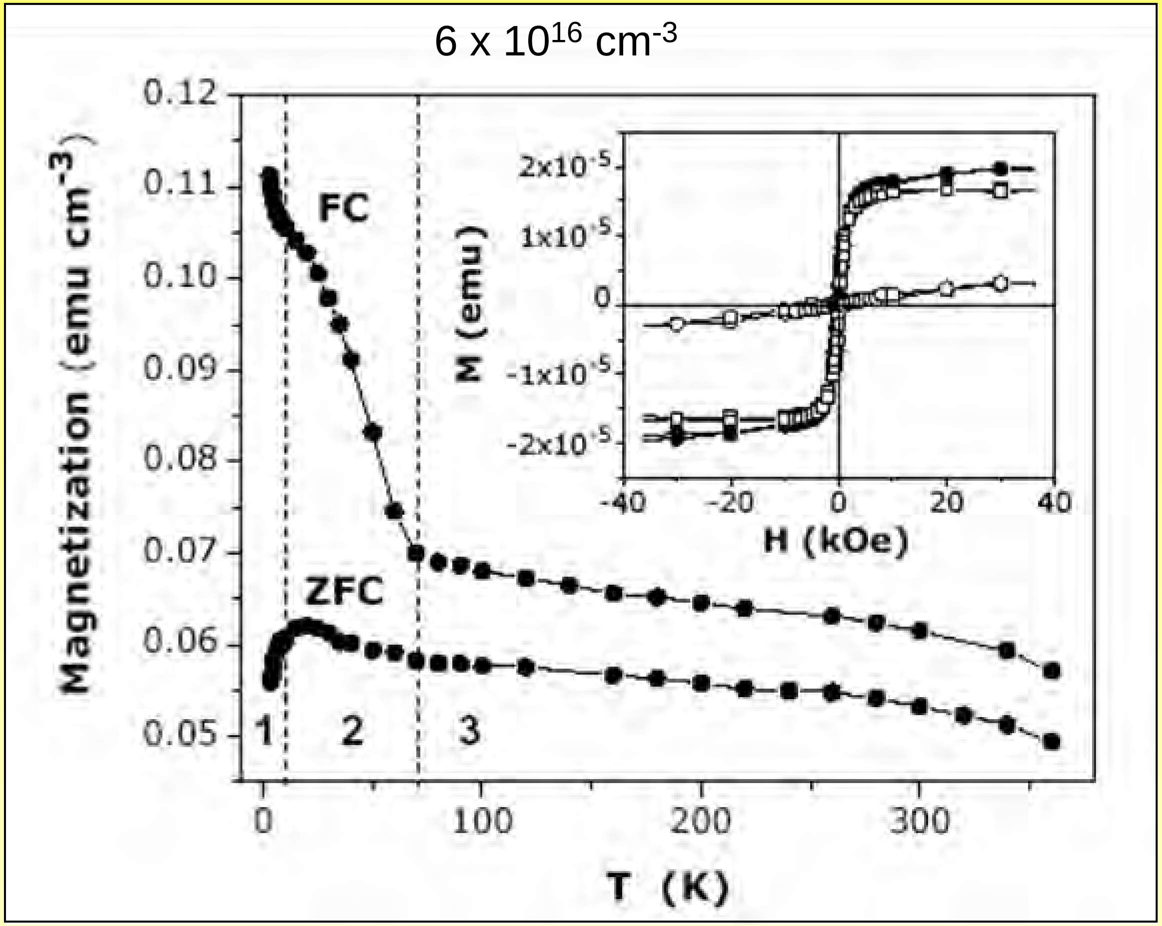
Average moment per Gd atom is as high as **4000 μ_B**

Fit parameter

2 K: $p_m = 1.1 \times 10^{-3}\ \mu_B$, $r = 33$ nm

300 K: $p_m = 8.4 \times 10^{-4}\ \mu_B$, $r = 28$ nm

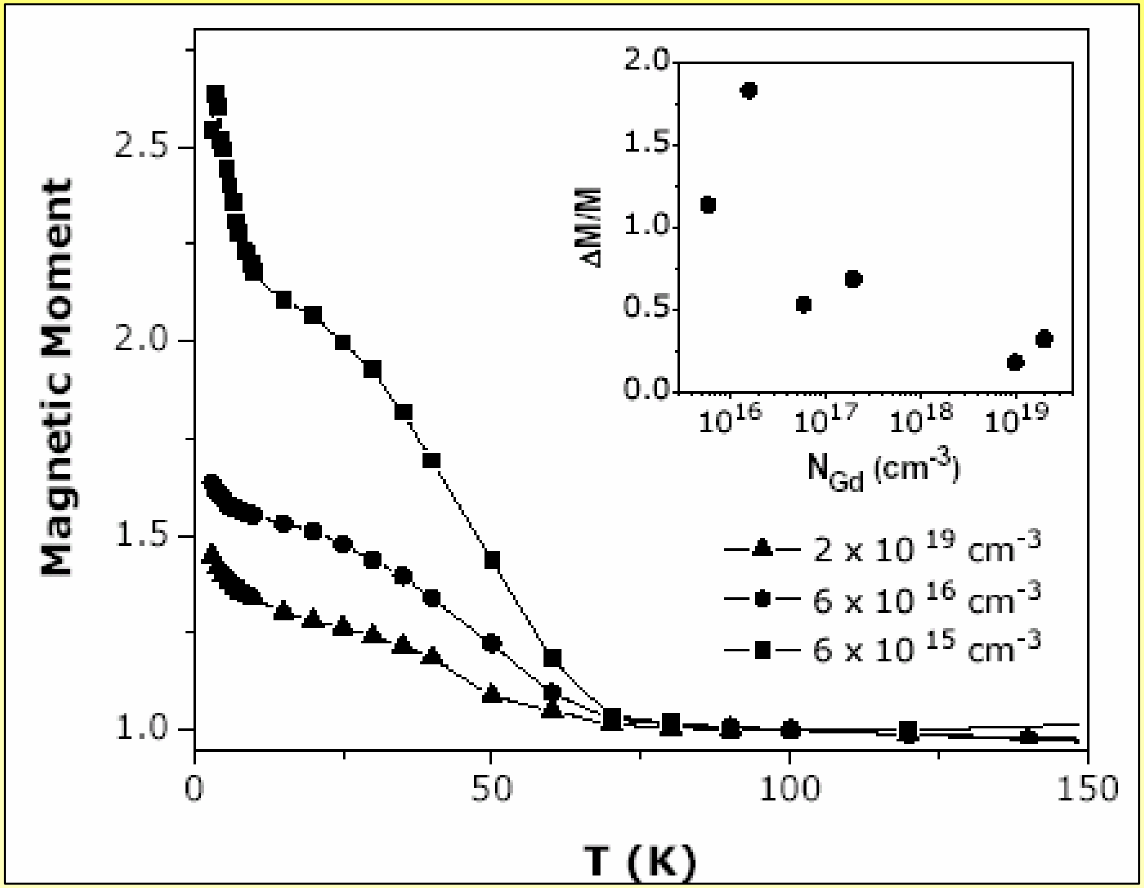
FC and ZFC curves from Gd-doped GaN



Temperature ranges 1,2,3 refer to three distinct magnetic contributions

Contribution 3 determines the Curie temperature

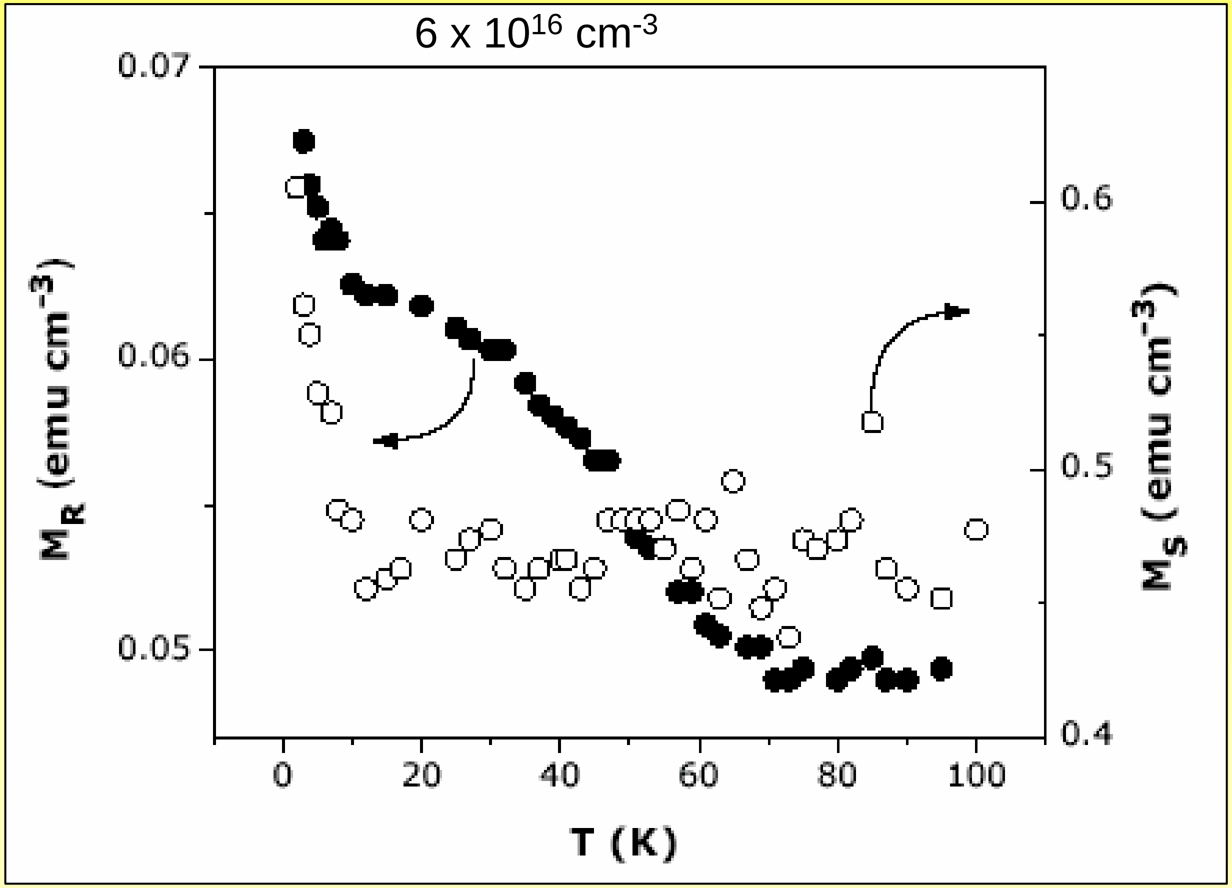
FC curves from GaN with different Gd concentration



Curves are normalized to 100 K values

Relative contribution of 70 K transition is reduced with Gd increase (see inset)

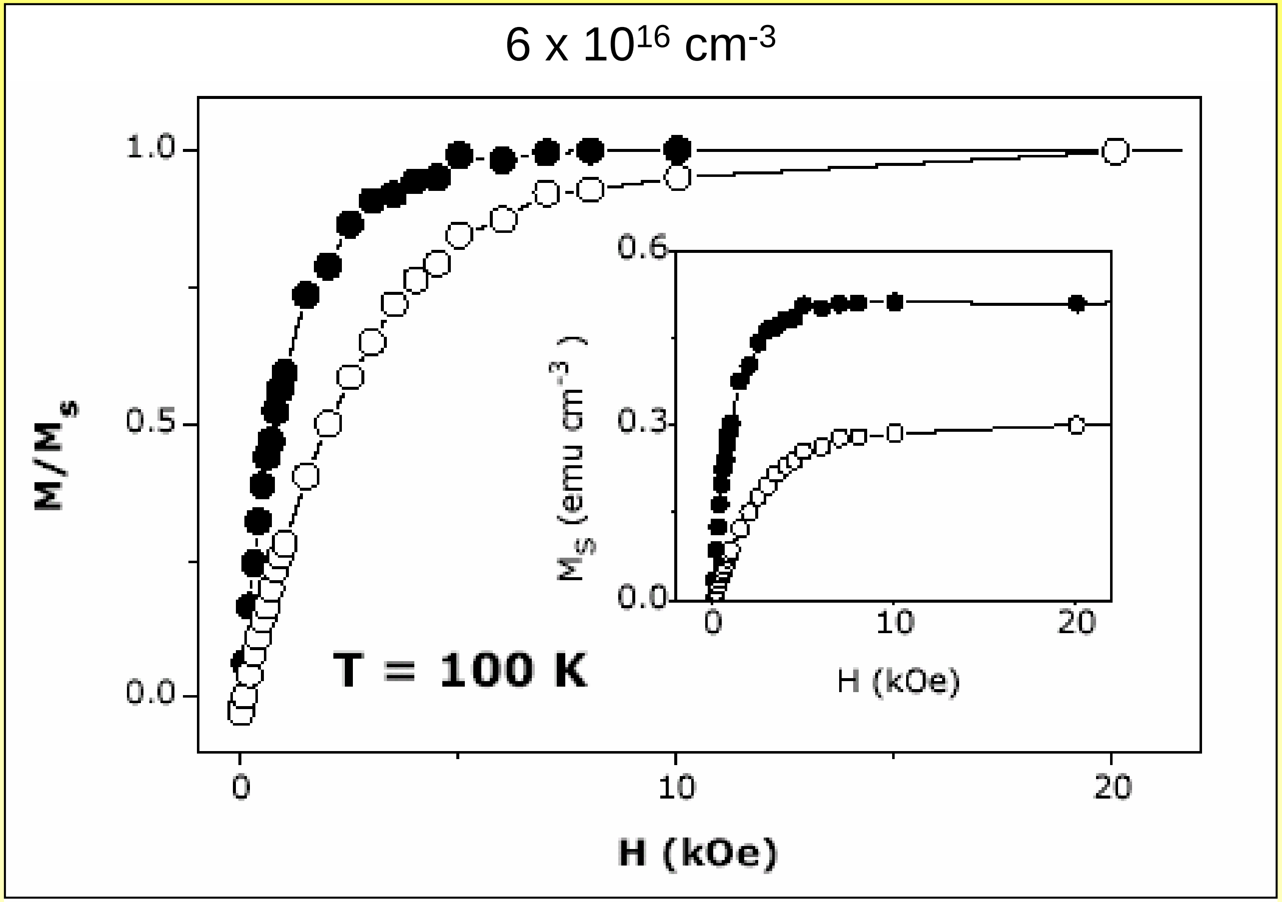
T-dependence of remance and saturation magnetization of Gd-doped GaN



Remanence shows two-step behavior at 10 and 70 K similar to the FC curves

Saturation magnetization shows only one step at 10 K

Magnetization curves of Gd-doped GaN measured in two perpendicular directions



Saturation magnetization is smaller along hard axis

Anisotropy energy for out-of-plane measurements is two times higher

Influence of defects on ferromagnetism in Gd-doped GaN

Do intrinsic and/or extrinsic defects play the role of „mediators“ in the inter-impurity exchange coupling between the Gd-ions ?

Experiments:

Focussed ion beam (FIB) implantation of 300 keV Gd-ions into GaN layers

Comparison of magnetic properties of as-implanted and annealed GaN:Gd samples

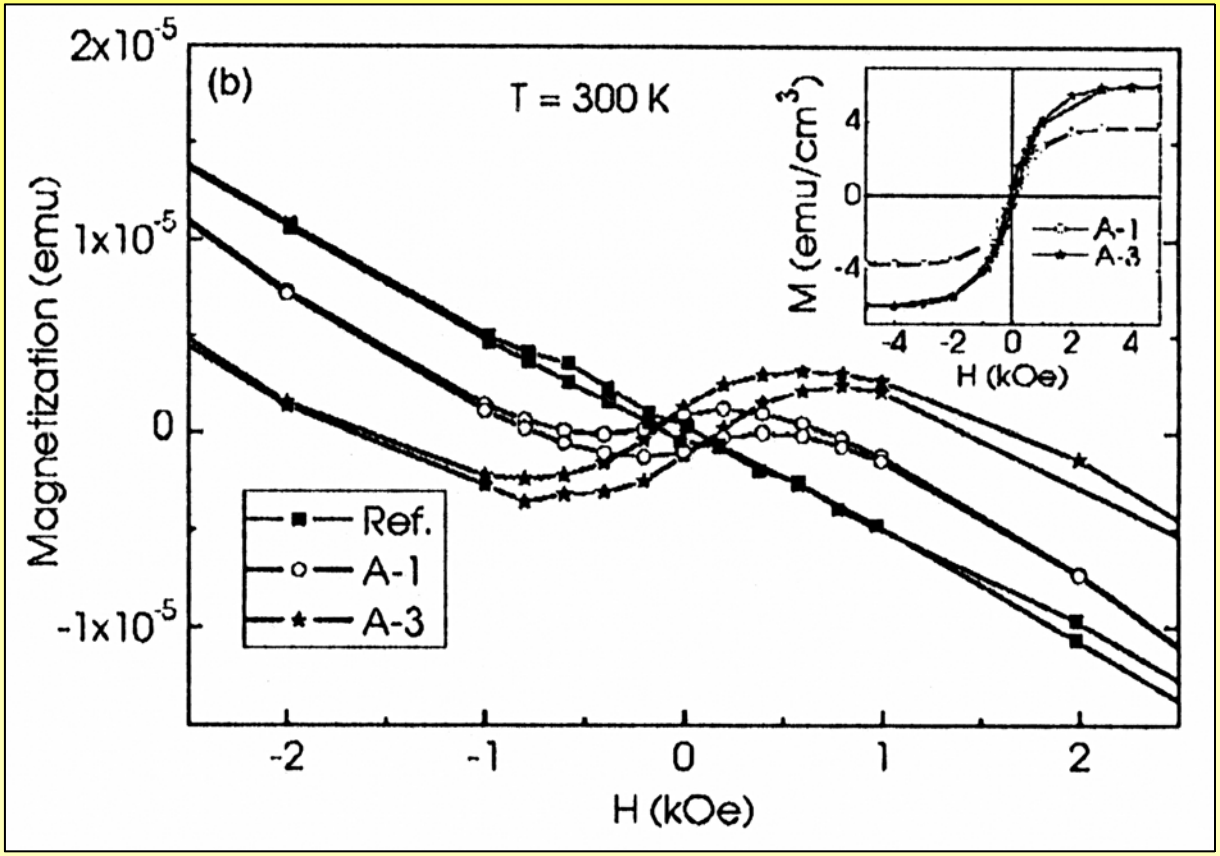
Theoretical model for intrinsic ferromagnetism without free carriers:

G. Cohen et al.

„Vacancy mediated ferromagnetic interaction in TiO_2 doped with magnetic ions“

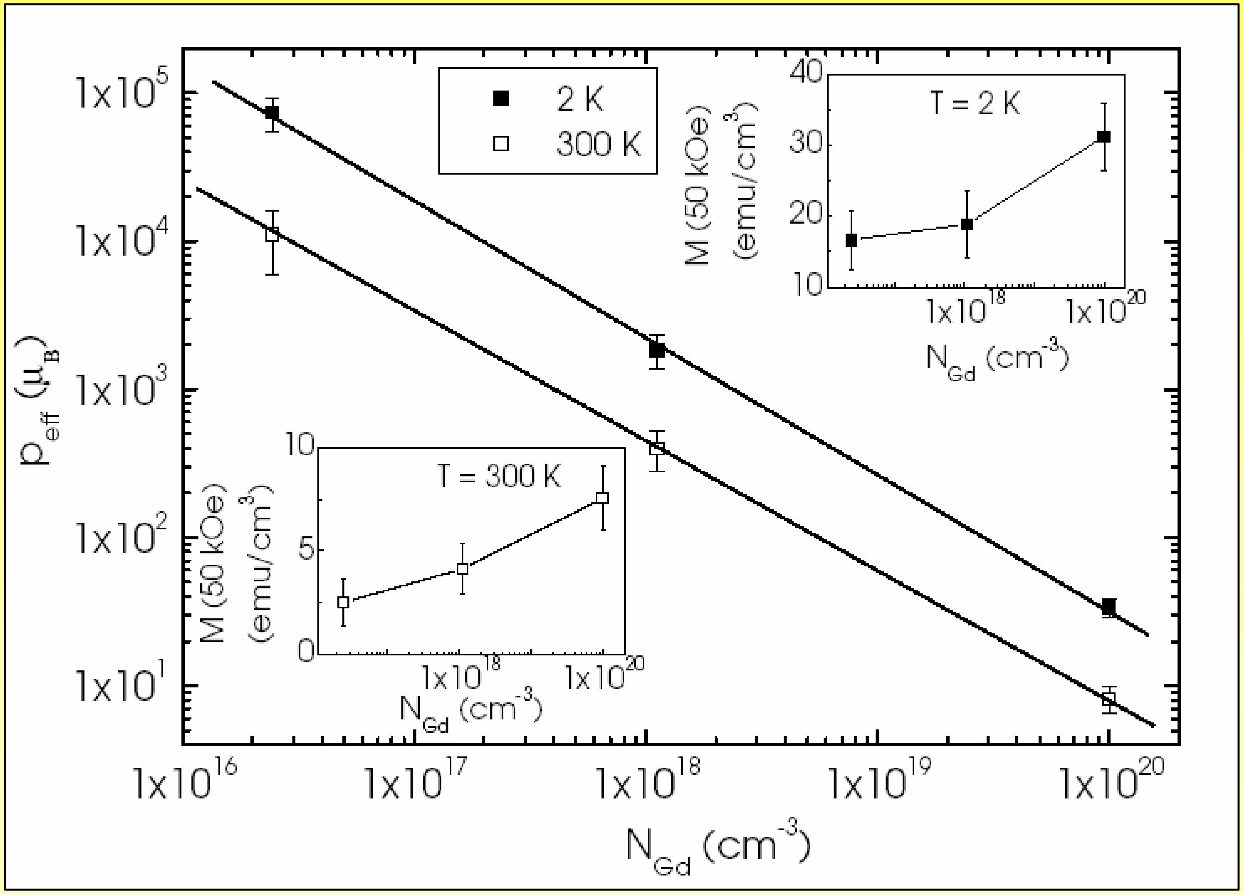
J. Appl. Phys. 101 (2007) 09H106

Magnetization loops from Gd-implanted GaN



Inset shows loops corrected for diamagnetic contribution from substrate

Magnetic moment of Gd in implanted GaN

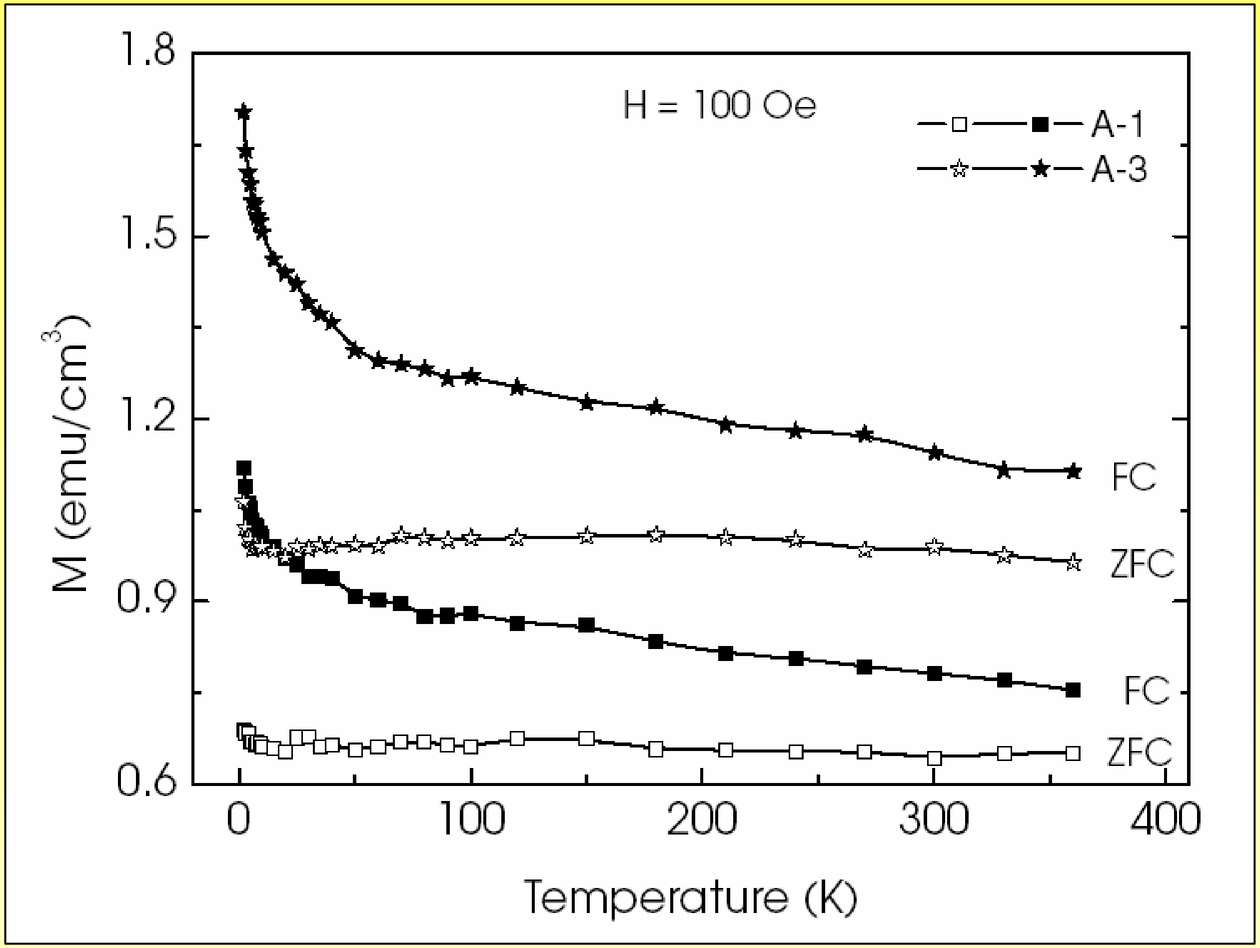


Value of magnetic moment per Gd atom derived from observed remanent magnetization

→ big change with temperature

Insets show observed magnetization as function of Gd concentration

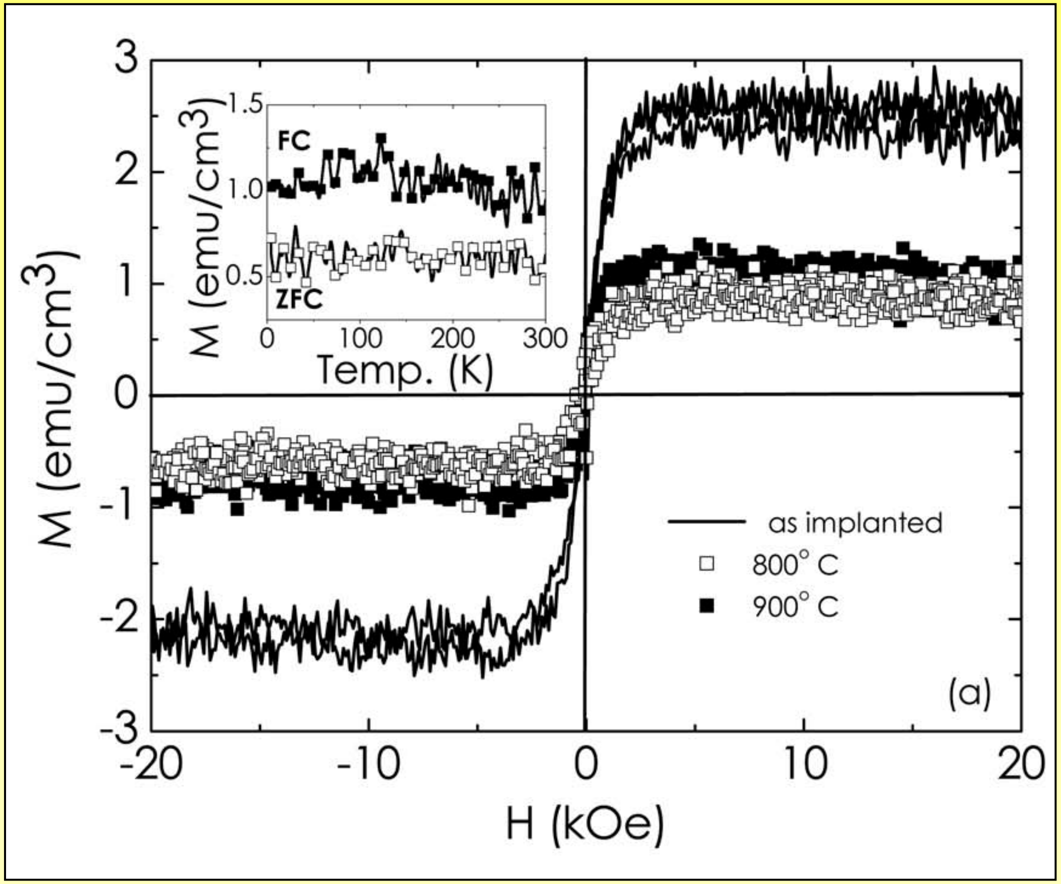
FC and ZFC magnetization in Gd-implanted GaN



Sample A-1: 2×10^{16} cm^{-3}

Sample A-3: 1×10^{20} cm^{-3}

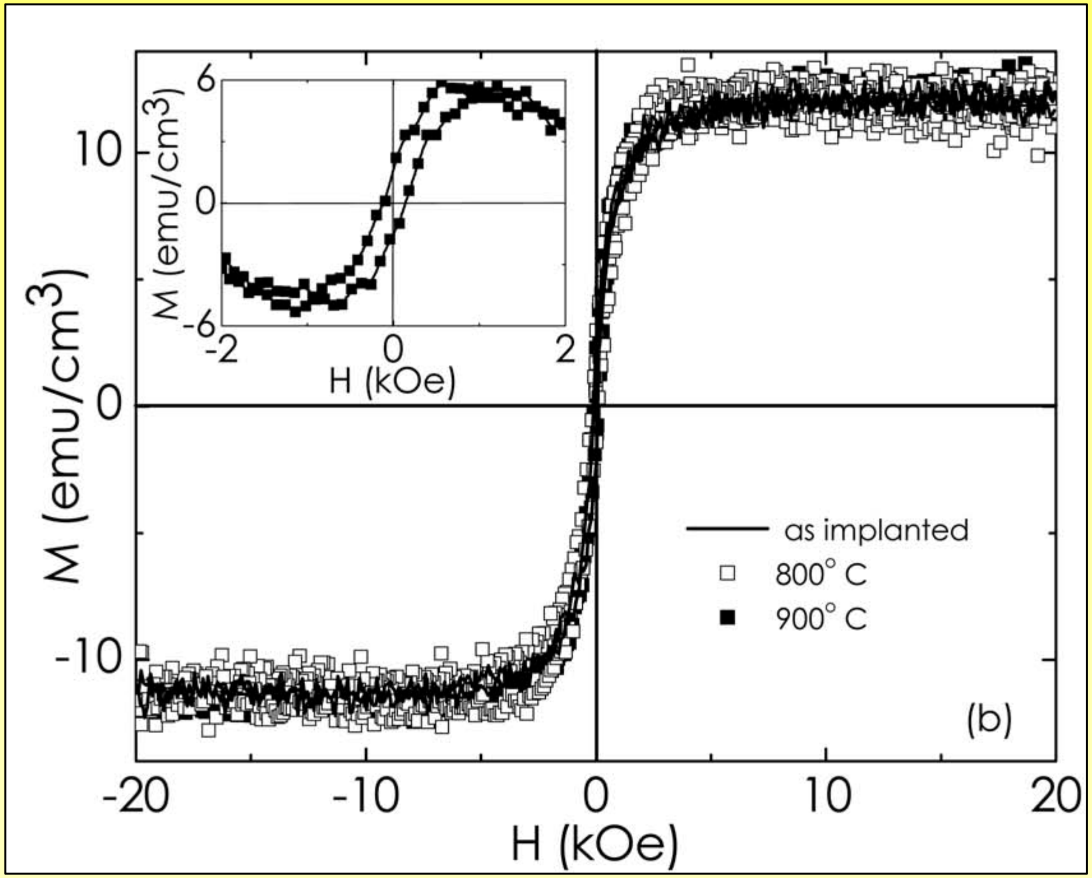
Effect of annealing on magnetization of Gd-implanted GaN (lower dose)



300 K magnetization curves before and after annealing (RTA)

Inset shows Fc and ZFC magnetization measured at 100 Oe

Effect of annealing on magnetization of Gd-implanted GaN (higher dose)



300 K magnetization curves before and after annealing (RTA)

Inset shows magnetization loop after annealing but before subtracting diamagnetic contribution from substrate

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Conclusions

- Gd-doped GaN films grown by R-MBE are ferromagnetic with Curie temperatures above 300 K
- Ferromagnetic Gd-doped GaN films are insulating and exhibit $(D^{(0)},X)$ features in photoluminescence
- Colossal magnetic moment per Gd atom is enhanced in Gd-implanted GaN films
- Structural defects may play important role as ‘mediators’ in the exchange coupling between the Gd impurities
- Empirical model based on polarisation of GaN matrix by Gd impurities explains
  - observed colossal magnetic moment,
  - observed co-existence of two ferromagnetic phases,
  - observed dependence of saturation magnetization on the orientation of the magnetic field
- More sophisticated theoretical models are needed to understand the mechanisms of the inter-impurity exchange coupling in ‘dilute magnetic dielectrics’ where free carriers are absent (see recent models for Co-doped $TiO_{(2)}$)

Acknowledgement

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