Ferromagnetic Semiconductors with high Curie Temperature and Unusual Magnetic Properties

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The case of Gd-doped GaN
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

4. Empirical model for colossal magnetic moment
   - Empirical model
   - Magnetic phases and anisotropy
   - Influence of defects on ferromagnetism

5. Conclusions
Spintronics

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

Electrical injection of polarized carriers

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“

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]


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

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 controversially discussed and often not reproducible.

In general, the actual exchange mechanism in ferromagnetic semiconductors is still a matter of controversy.
Magnetic semiconducting oxides

"Ferromagnetism in epitaxial (Zn,Co)O films grown on ZnO and Al₂O₃."

T. Fukumura, H. Toyosaki, and Y. Yamada
„Magnetic oxide semiconductors“

S. J. Pearton, W. H. Heo, M. Ivill, D. P. Norton and T. Steiner
„Dilute magnetic semiconducting oxides“

S. A. Chambers and R. F. C. Farrow
„New possibilities for ferromagnetic semiconductors“
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........


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 → 623 nm emission
  - Er-doped GaN → 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

- 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 → new coupling mechanism?

Ref:
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Growth of Gd-doped GaN

- Reactive (NH₃) molecular beam epitaxy (R-MBE)
- 4N (99.00%) Gd ingots from Stanford Mater. Corp.,
- Tₑ = 950 - 1300° C (→below melting point of Gd)
- 6H-SiC(0001) substrates, Tₛ = 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 10¹⁹ 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 ($\omega - 2\theta$ scan)

- 300“ width for symmetric (0002) reflection
- 900“ width for asymmetric (1105) reflection
X-ray diffraction ($\omega - 2\theta$)

No secondary phase detected
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 ⇒ Ferromagnetism

Superposition of two loops with different $H_c$ and $M_r$ at 2 K?
→ above 10 K phase with larger $H_c$ and $M_r$ disappears
Details of hysteresis curves

![Graph showing hysteresis curves for different samples at T = 300 K. Arrows indicate the value of $M_r$.](image)

- Implanted GaN
- Sample G
- Sample C
- Sample A

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 moment at 2 K per Gd atom is as high as $4000 \, \mu_B$

Values are obtained from the measured magnetization and the measured concentration.
Regime I: $M_s$ increases with $[Gd]$ up to percolation threshold
Regime II: $M_s$ is independent of $[Gd]$ and $\rho_{eff}$ decreases with $[Gd]$
Regime III: $M_s$ increases again with $[Gd]$ and $\rho_{eff}$ approaches saturation
Probing of Gd L₃ 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
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^0,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^0,X) distance ≈ 12 nm

⇒ Gd has a long-range influence on the GaN matrix
Relative change of the polarization increases with $N_{\text{Gd}}$

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

\[ p_e = p_{Gd} + p_m \nu \frac{N_o}{N_{Gd}}; \quad \nu = 1 - \exp(-\nu N_{Gd}) \]

\( p_e \) 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

\[ M_s = p_{Gd} N_{Gd} + p_0 \tilde{\nu} N_0 + p_1 N_0 \sum_{n=2}^{N_{Gd}} n \tilde{\nu}_n \]

\( N_0 \) = concentration of matrix atoms per unit volume
\( \nu \) = volume of each sphere

\[ \tilde{\nu}_n = \left( \frac{\nu N_{Gd}}{n!} \right)^n e^{-\nu N_{Gd}} \]

Volume fraction of the regions contained within \( n \) spheres

Average effective magnetic moment per Gd atom

\[ p_{eff} = p_{Gd} + p_1 N_0 \nu + \left[ p_0 - (p_0 + p_1 N_{Gd} \nu) e^{-\nu N_{Gd}} \right] \frac{N_0}{N_{Gd}} \]
Fit of experimental $M_s$ vs $N_{Gd}$ data

$p_{Gd} = 8 \mu B$

Fit parameter

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_0$</td>
<td>$1.1 \times 10^{-3} \mu B$</td>
</tr>
<tr>
<td>$8.4 \times 10^{-4} \mu B$</td>
<td></td>
</tr>
<tr>
<td>$p_1$</td>
<td>$1.0 \times 10^{-5} \mu B$</td>
</tr>
<tr>
<td>$\approx 0$</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>33 nm</td>
</tr>
<tr>
<td>$28$ nm</td>
<td></td>
</tr>
</tbody>
</table>

Three regimes in $M_s$ vs $N_{Gd}$ curve:

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

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

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

→ $M_s$ independent on $N_{Gd}$
→ $p_{eff}$ decreases with $N_{Gd}$

III. Entire GaN matrix is polarized

→ First term of equation dominates, i.e. $M_s$ increases with $N_{Gd}$
→ $p_{eff}$ starts to saturate (value by amount of $p_1N_0\nu$ larger than 8 $\mu B$)
Average moment per Gd atom is as high as $4000 \ \mu_B$

Fit parameter

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

300 K: $p_m = 8.4 \times 10^{-4} \ \mu_B$, $r = 28 \text{ nm}$
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)
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 TiO₂ doped with magnetic ions“
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 x 10^{16} \text{ cm}^{-3}
Sample A-3: 1 x 10^{20} \text{ 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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- 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 Ti\(\text{O}_2\))
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