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OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Are Rare-Earth Nitrides the Future of Spintronics?

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VICTORIA UNIVERSITY OF WELLINGTON
Te Whare Wananga o te Upoko o te Ika a Maui

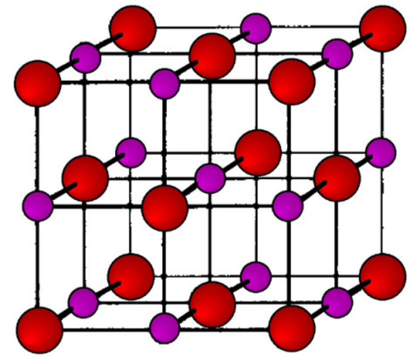
The MacDiarmid Institute
for Advanced Materials and Nanotechnology

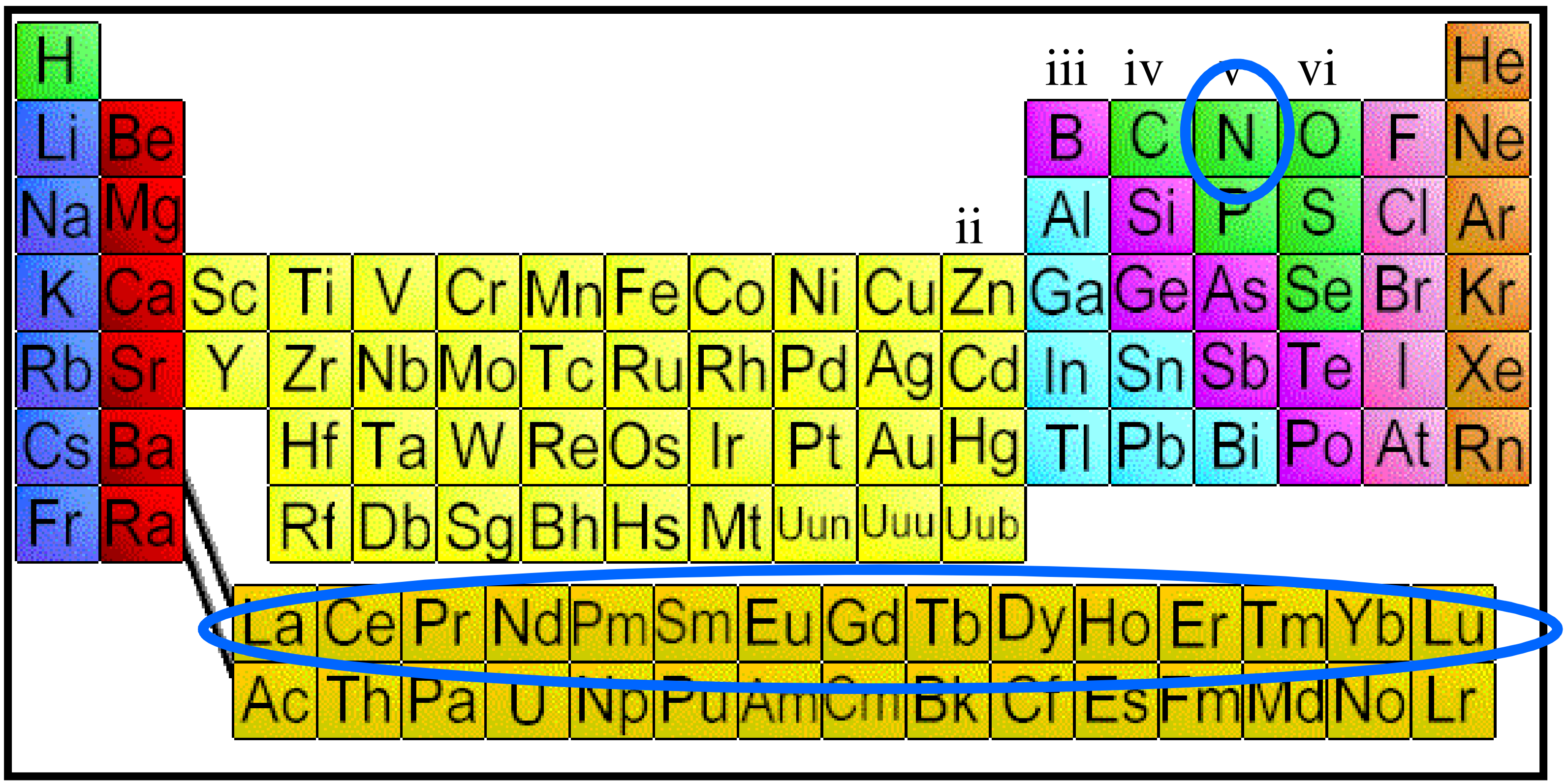
Outline

- Motivation, why are they interesting?
- Epitaxial film growth
- Properties of (some) RENs
- Conclusion & perspectives

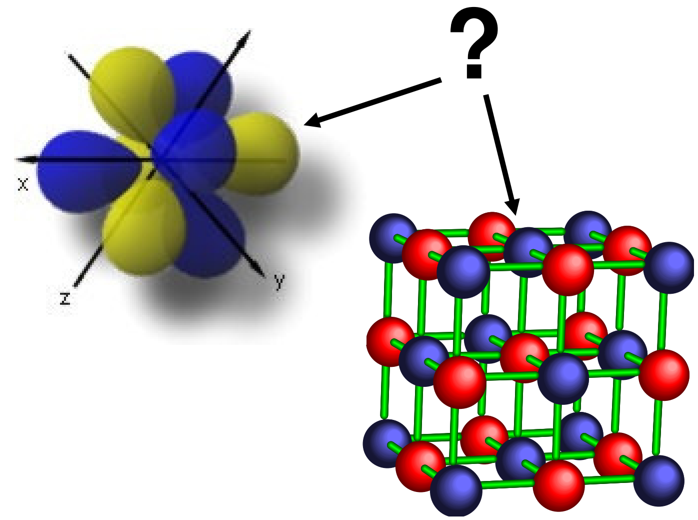
Rare-earth nitrides

- 15 rare earth mononitrides (RE-N).
- Rocksalt structure.
- Trivalent RENs; RE^{3+}/N^{3-}
- Unstable in air: oxidation to RE_2O_3





Rare-earth nitrides



- Strongly correlated 4*f* electrons:
  - *Simple rocksalt structure* $RE^{3+}N^{3-}$
  - *Band picture vs. atomic picture?*
- Magnetism:
  - *Orbital and spin moments*
  - *Contrasting magnetic properties*
- Semiconductors or half-metals?
- Experimental picture murky (N vacancies, decomposition in air)
- Spintronics?

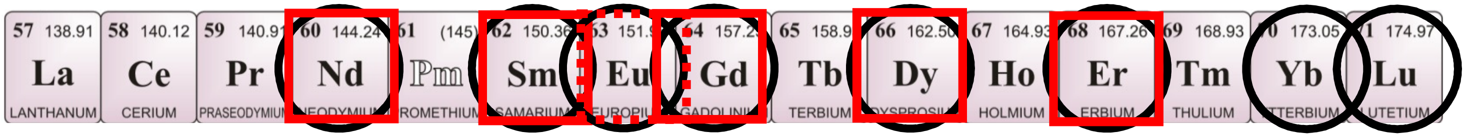
History of rare-earth nitrides

- RE nitrides were studied in the 1960-1970s
- Stoichiometry poor (N vacancies, O contamination)
- Ferromagnetic structure known for most
- Almost nothing was known about the electronic band structure

- Theoretical interest strong since ~ 2000
- Experimental activities since ~2006

57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.05	71 174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERBIUM	LUTETIUM

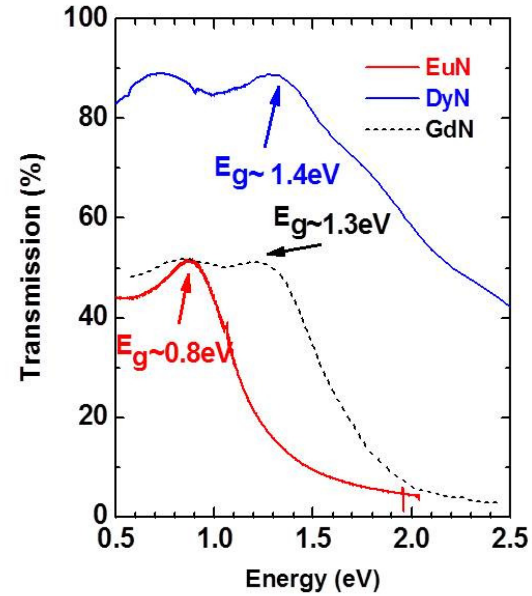
Rare-earth nitrides



semiconductors

Ferromagnetic

Optical Band Gap from ~0.7eV to ~1.8eV

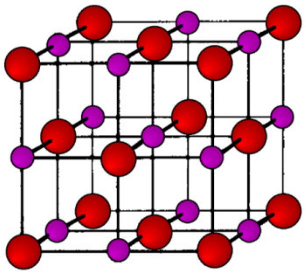


- Intrinsic ferromagnetic semiconductors : Eu chalcogenides (EuO, EuS…) and rare-earth nitrides

Magnetic ions are NOT introduced into a non-magnetic semiconductor host: every cation is magnetic
⇒ independent control of the carrier concentration (doping) and magnetism
Novel class of electronic technology: semiconductor-spintronic!!!

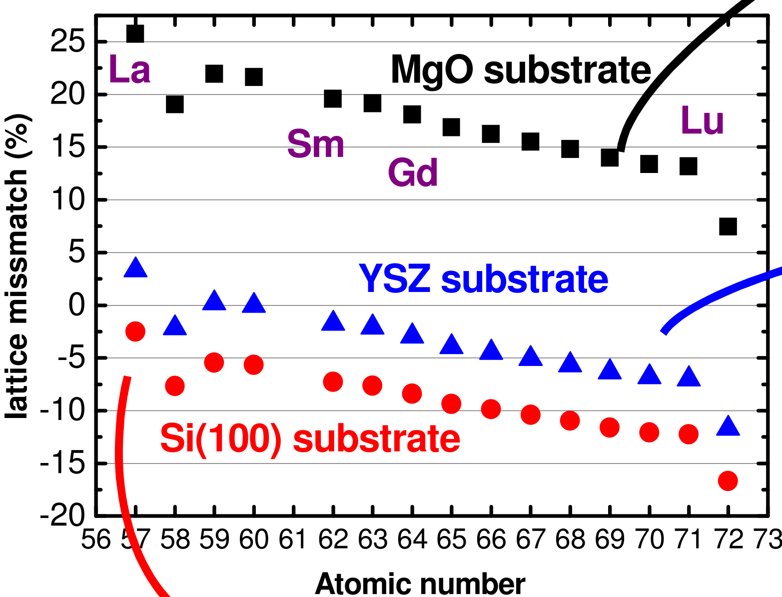
F. Natali et al., "Rare-earth mononitrides", Progress in Materials Science 58, 1316 (2013)

Epitaxial growth on (100) surfaces



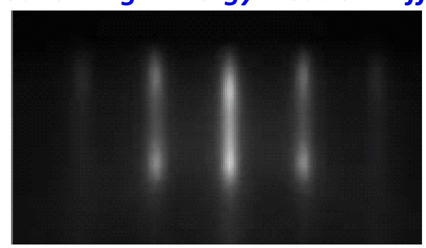
GdN a = 4.974 Å
EuN a = 4.8 Å
SmN a = 5.035 Å

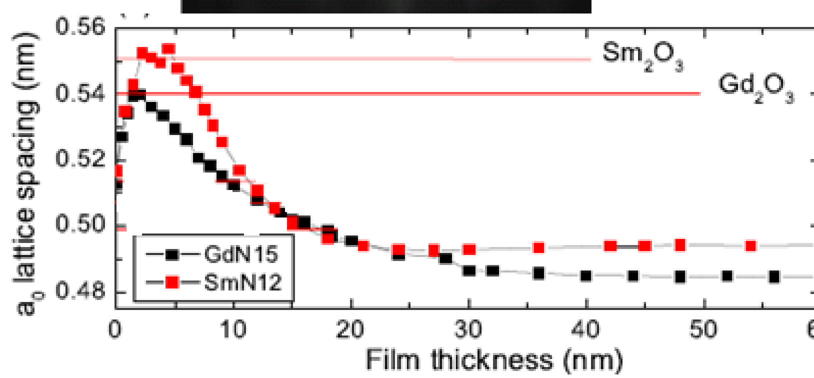
First epitaxial growth GdN(100) on MgO
Appl. Phys. Lett. **90**, 061919 (2007)



SmN on YSZ by PLD

Reflection High-Energy Electron Diffraction



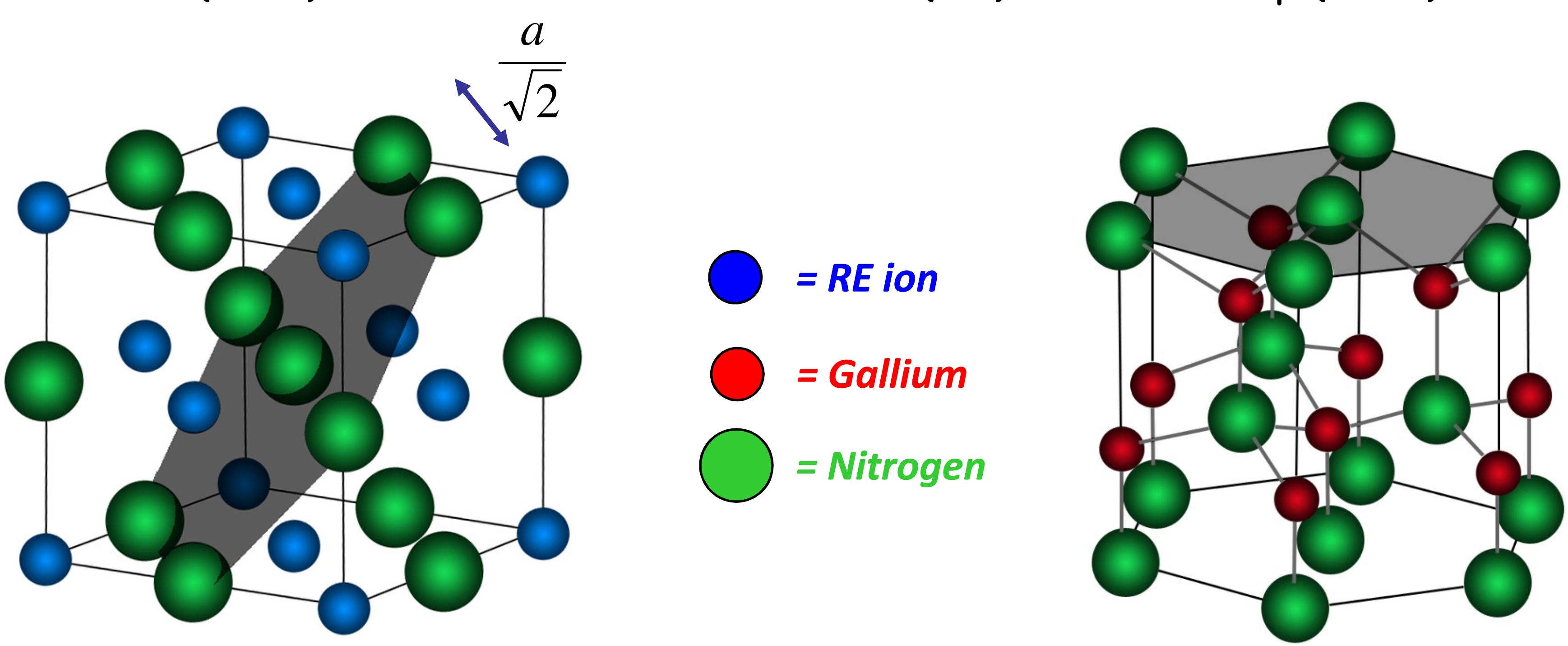


NEED a growth procedure layer to prevent RE and Si diffusion
⇒ **formation of rare-earth silicide compounds**

Ludbrook *et al.*, J. Appl. Phys. **106**, 063910(2009)
F. Natali *et al.*, Phys. Status Solidi C **9**, 605 (2012)

Epitaxial growth: combining rare-earth nitrides and group-III nitrides

Rocksalt (NaCl) structure $Re^{3+}N^{3+}$ - Rocksalt (111) surface ≡ hcp (0001) surface



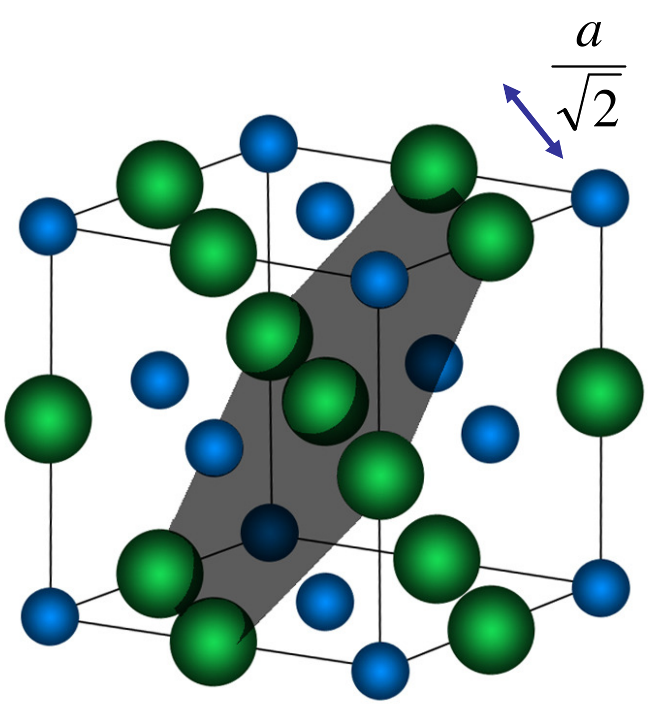
Rocksalt RE-nitrides *Hexagonal III-nitrides*

Indirect Semiconductors
Band Gap from ~0.7eV to ~1.8eV
Lattice parameter ~5 Å

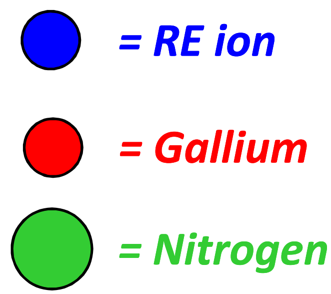
Direct Semiconductor
Band Gap from ~6.2eV to ~0.8eV
Lattice parameter ~3.15 Å

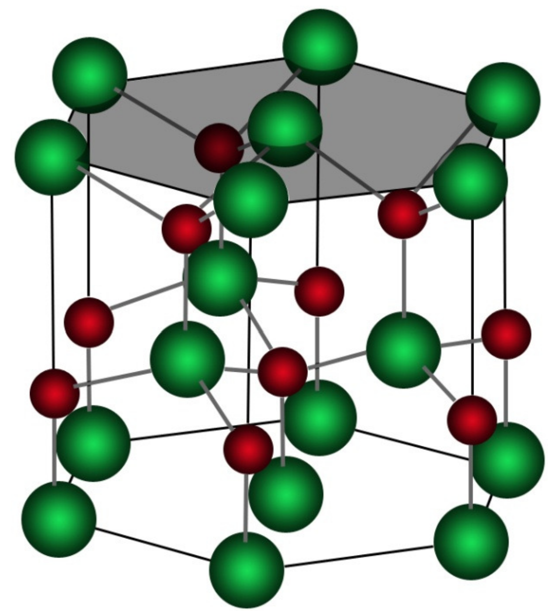
Epitaxial growth: combining rare-earth nitrides and group-III nitrides

Rocksalt (NaCl) structure $Re^{3+}N^{3+}$ - Rocksalt (111) surface ≡ hcp (0001) surface



Rocksalt RE-nitrides



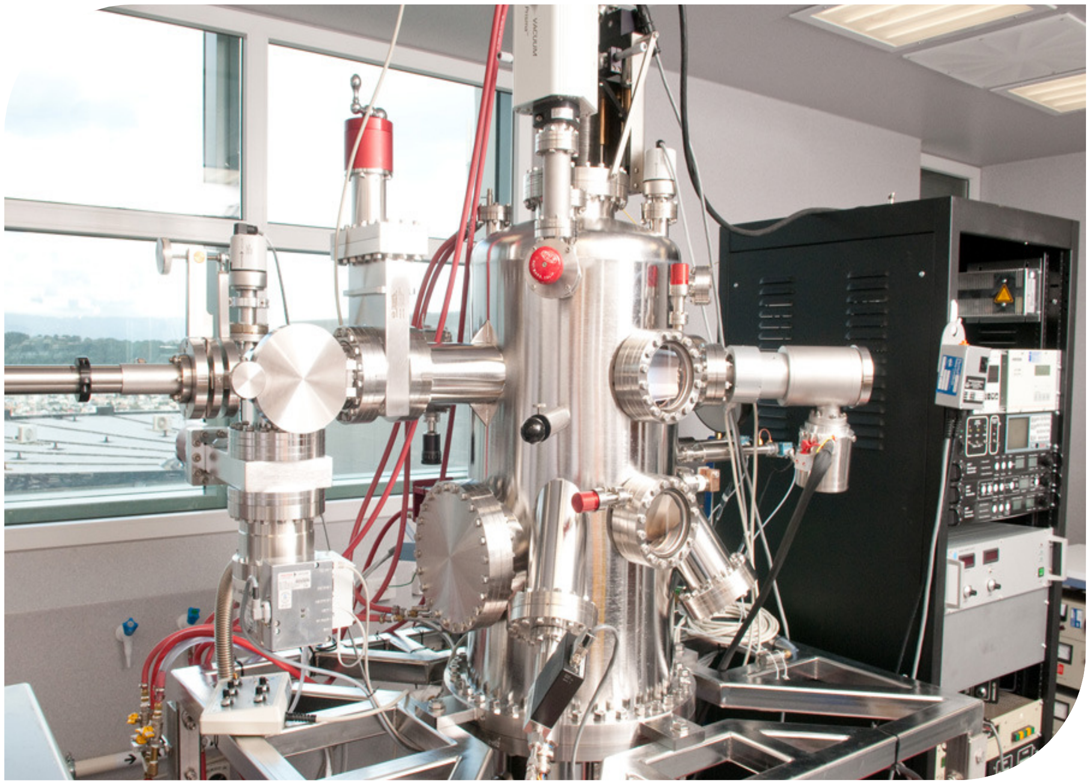


Hexagonal III-nitrides

RE-N {111} on III-N {0001} Lattice Mismatch (%)

	$a\sqrt{2}/2$	AlN	GaN	InN	Si(111)
GdN	3.518	13	10.3	-0.85	-8.38
EuN	3.522	13.2	11.3	0	-7.59
SmN	3.56	14.4	11.66	0.36	-7.26

Molecular beam epitaxy



The films are grown by deposition of the RE in the presence of NH_3 or N_2 :

-pure N_2 and sometimes activated nitrogen
-RE thermal evaporation
-Characterisation by RHEED
-Passivation AlN/GaN cap layers
-ambient T for polycrystalline films
-high-temperature for epitaxial growth, 2" substrate holder.
-Base pressure : $<10^{-8}$ Torr
-Press. Process : 10^{-5}- 10^{-4} Torr

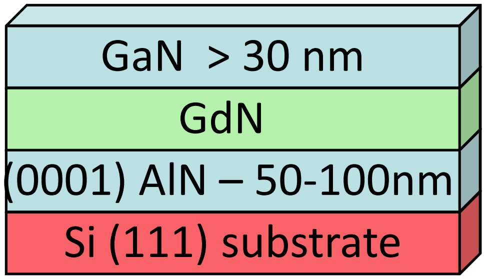
To date: GdN, SmN, DyN, ErN, EuN, LuN, NdN, YbN

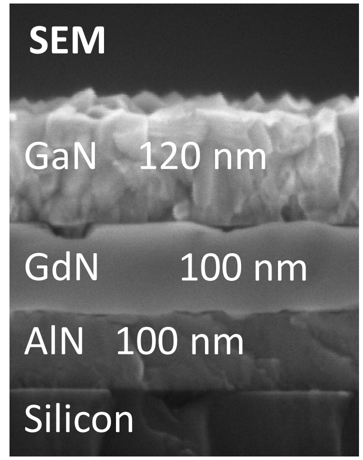
Molecular beam epitaxy

Structure & Growth Conditions:

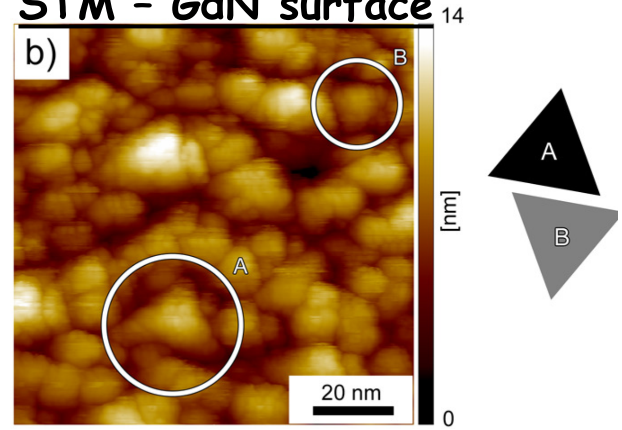
N_2/NH_3 flux = 10^2-10^3 Gd flux

Vg = 120nm/h - Tg = 470-850°C





STM – GdN surface



Twin islands

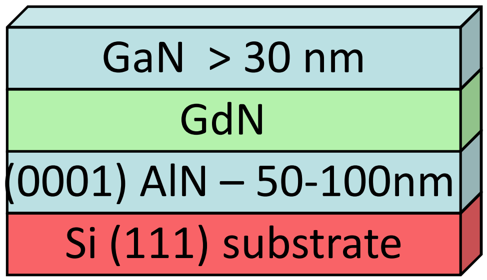
Two GdN in-plane orientations

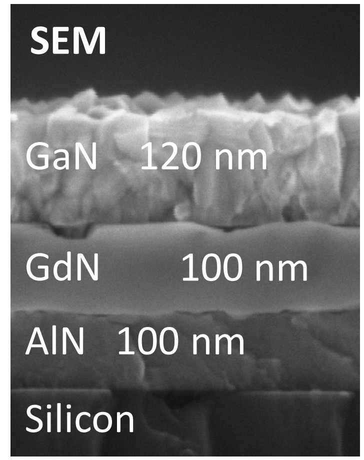
Molecular beam epitaxy

Structure & Growth Conditions:

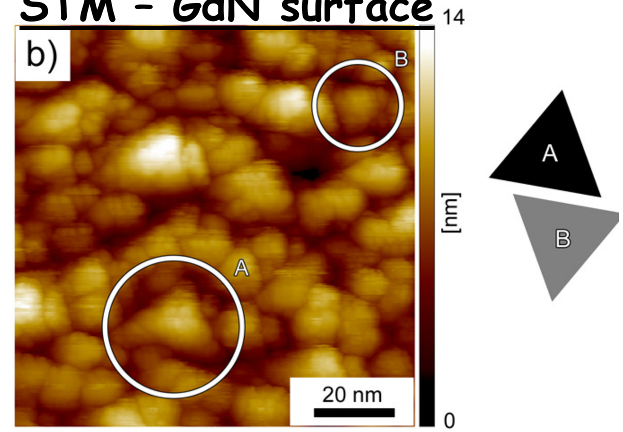
N_2/NH_3 flux = 10^2-10^3 Gd flux

Vg = 120nm/h - Tg = 470-850°C





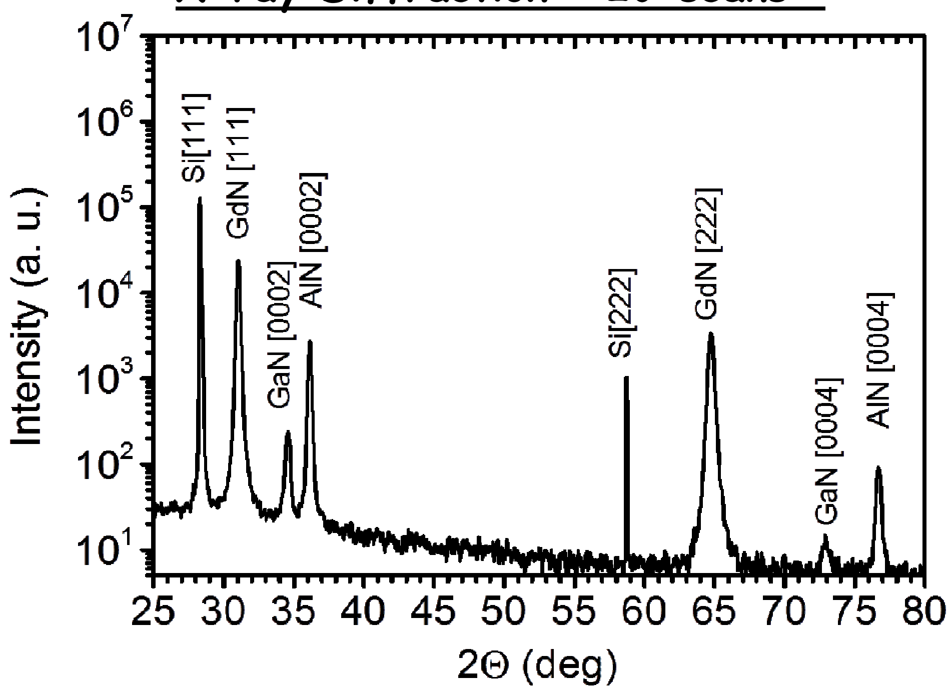
STM – GdN surface



Twin islands

Two GdN in-plane orientations

X-ray Diffraction : 2θ-scans



GdN (111) epitaxial on AlN (0001)

GdN (111) // AlN (0001)

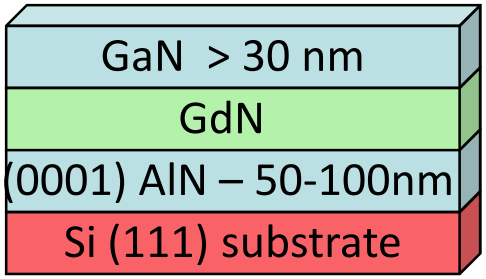
⇒AlN's hexagonal face favours a fully (111)-oriented GdN film.

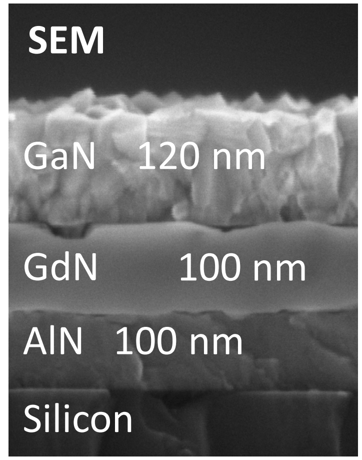
Phi-scan : 6 fold symmetry of GdN (002) reflections (not shown)

Molecular beam epitaxy

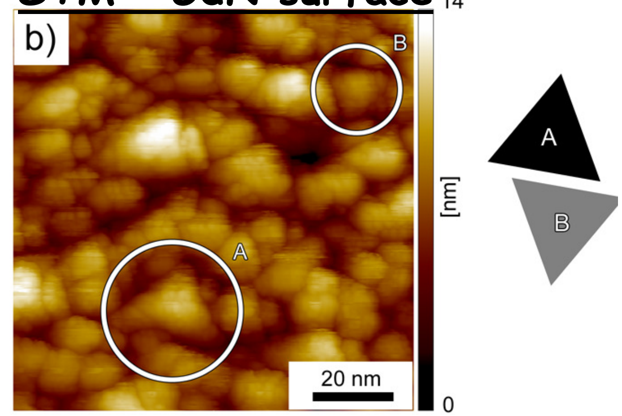
Structure & Growth Conditions:

N_2/NH_3 flux = 10^2-10^3 Gd flux
Vg = 120nm/h - Tg = 470-850°C



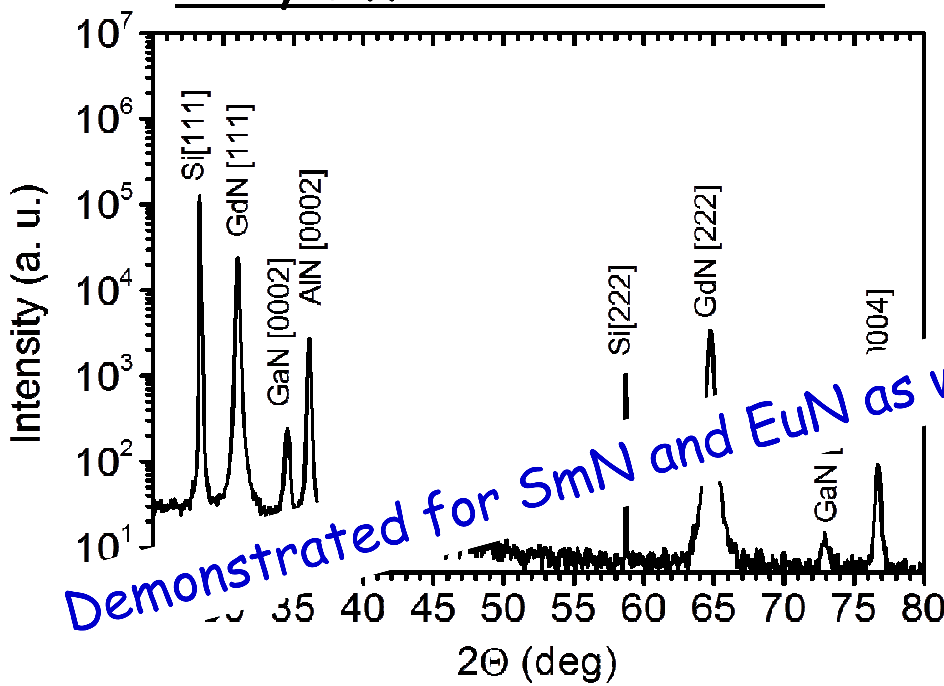


STM – GdN surface



Twin islands
Two GdN in-plane orientations

X-ray Diffraction : 2θ-scans



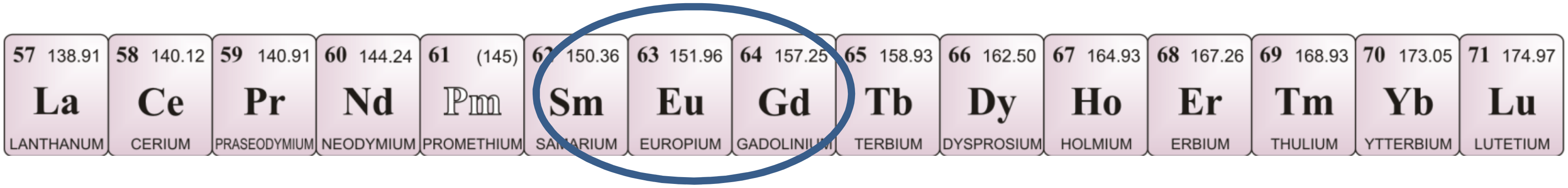
GdN (111) epitaxial on AlN (0001)
GdN (111) // AlN (0001)

⇒AlN's hexagonal fa... ...s a fully (111)-ori... ...N film.

Demonstrated for SmN and EuN as well on AlN and GaN surfaces!!!

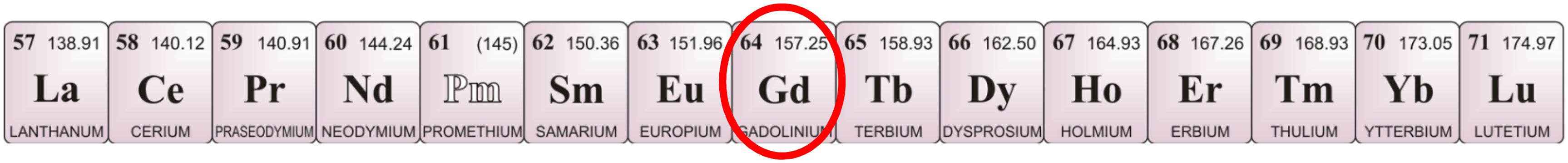
Phi-scan : 6 fold symmetry of GdN (002) reflections (not shown)

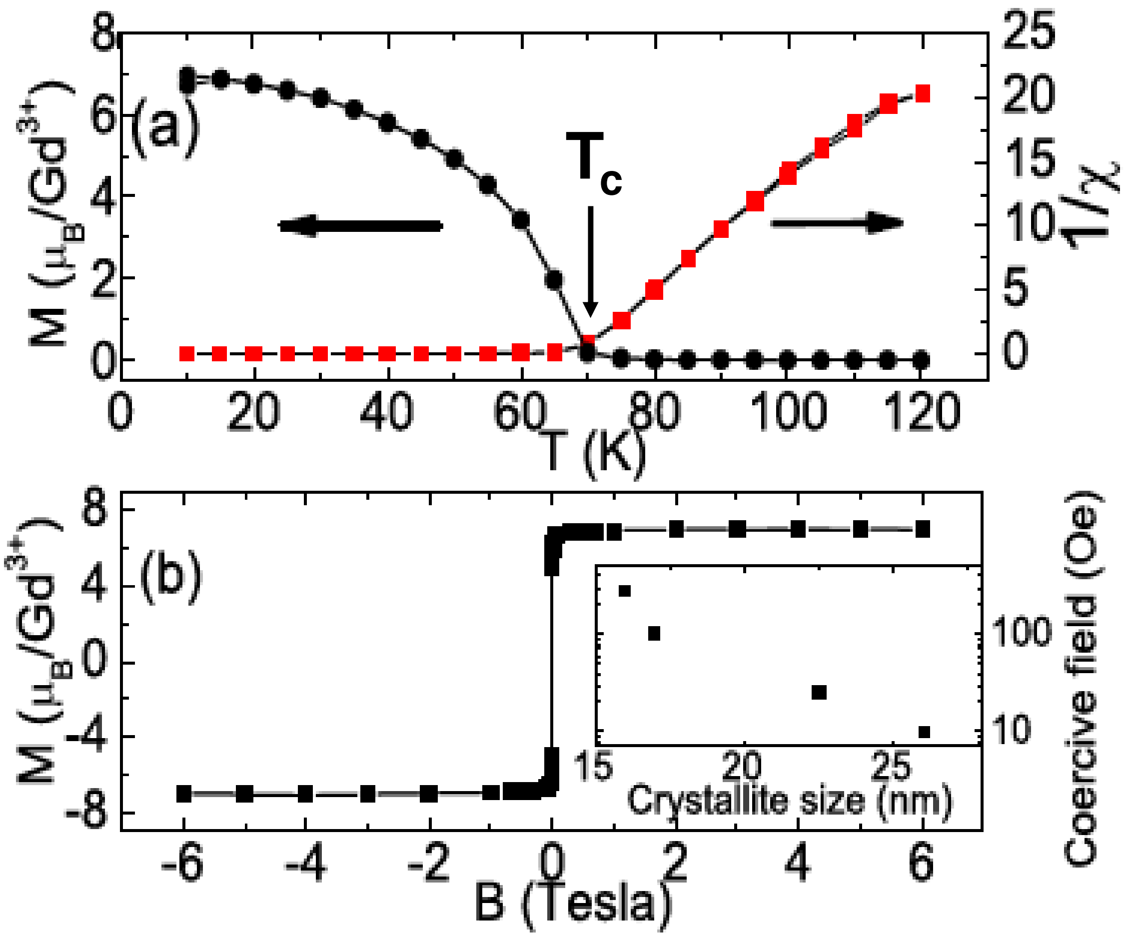
Rare-earth nitrides: properties



So far the most studied have been : GdN, SmN and EuN

Rare-earth nitrides: GdN



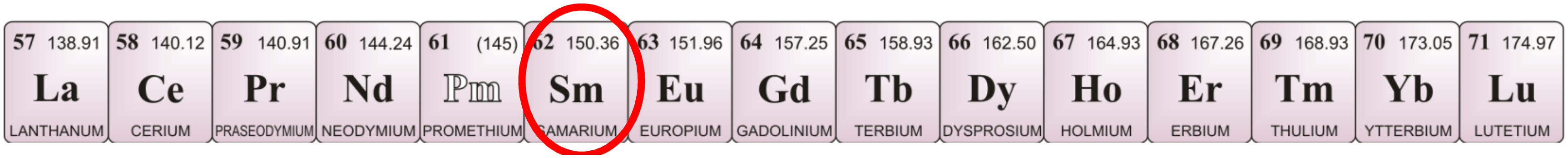


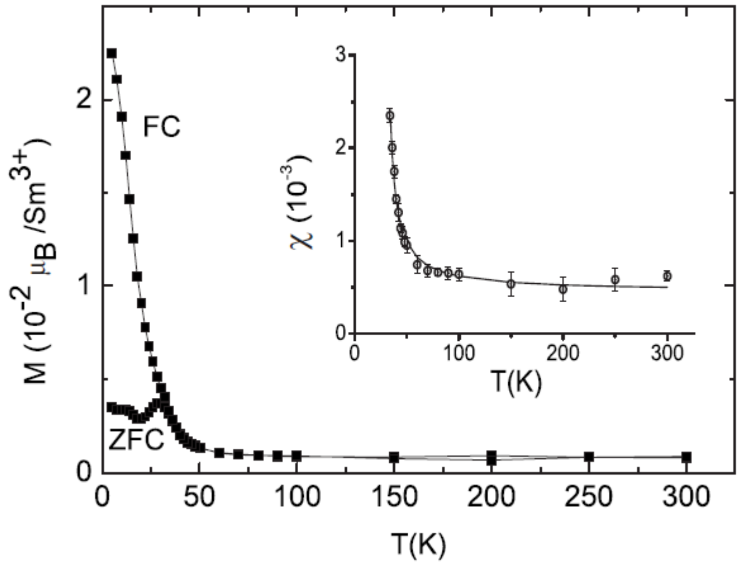
Noteworthy elements:

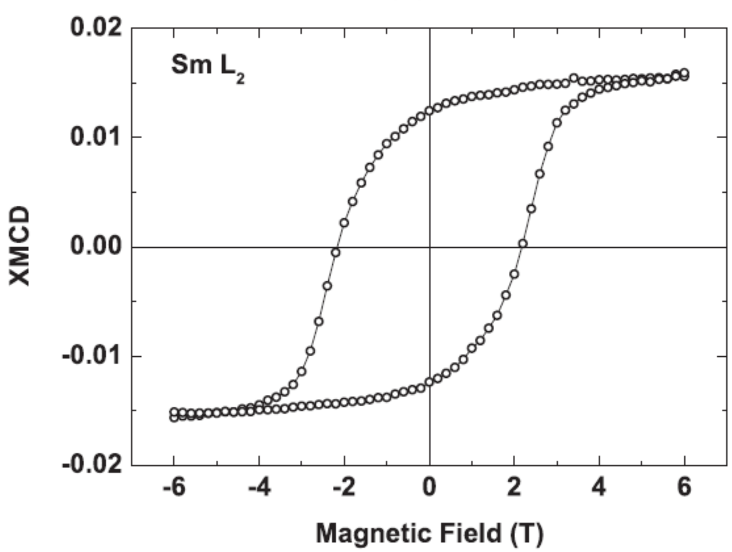
- Tc of 70 K (the largest among the RENs)
- 7 Bohr magnetons/Gd^{3+}
- remarkably small coercive field (<0.05 Tesla)

Ludbrook et al., J. Appl. Phys. 106, 063910 (2009) - F. Natali et al., J. Cryst. Growth 312, 3583 (2010)

Rare-earth nitrides : SmN





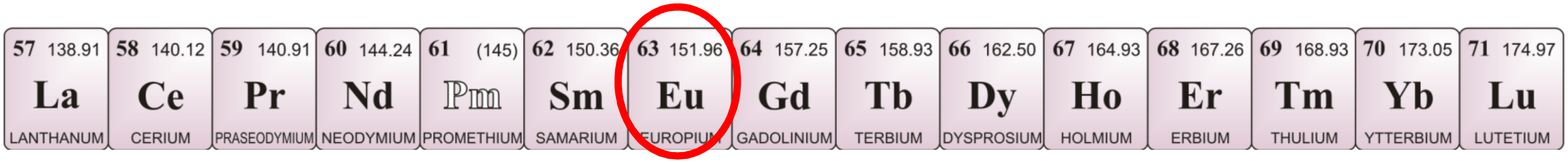


Noteworthy element:

- Only near-zero moment ferromagnetic semiconductor. Spin and orbital moments nearly cancel
- m_{tot} ~0.03 Bohr magnetons/Sm^{3+}
- T_c=27K.
- coercive field of >2 Tesla at 15K signaling the weak coupling of the small net moment to an external field.

C. Meyer et al., Phys. Rev. B 78, 174406 (2008)

Rare-earth nitrides: EuN



So far the most studied have been : GdN, SmN and EuN

PRL **111**, 167206 (2013) PHYSICAL REVIEW LETTERS week ending 18 OCTOBER 2013

Europium Nitride: A Novel Diluted Magnetic Semiconductor

Do Le Binh,[1] B. J. Ruck,[1,*] F. Natali,[1] H. Warring,[1] H. J. Trodahl,[1] E.-M. Anton,[1] C. Meyer,[2] L. Ranno,[2] F. Wilhelm,[3] and A. Rogalev[3]

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[3]*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex, France*

(Received 30 June 2013; published 18 October 2013)

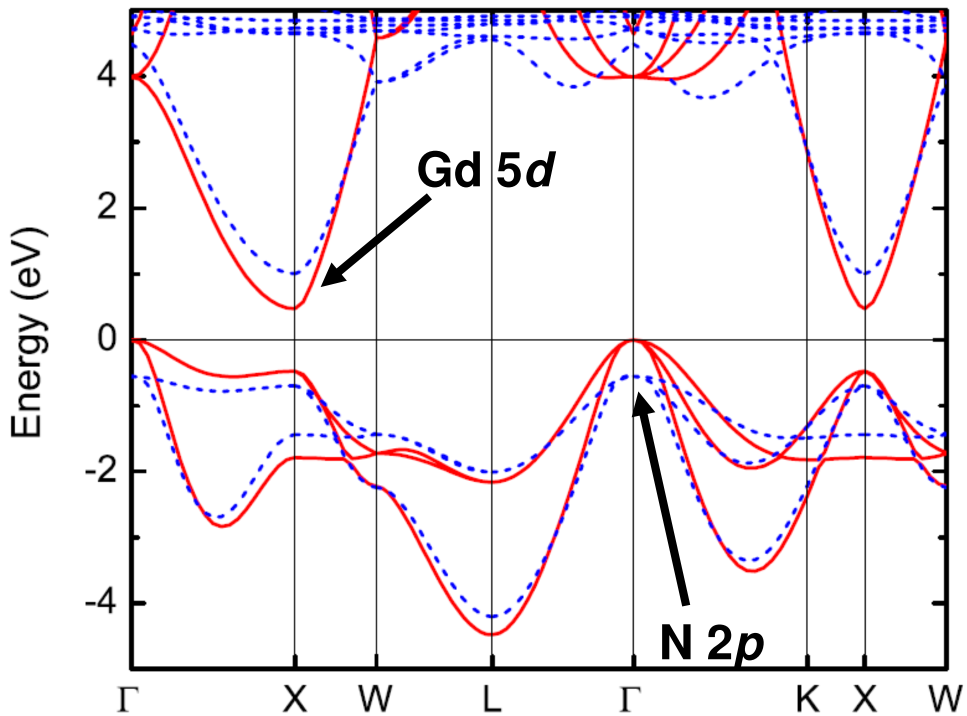
Europium nitride is semiconducting and contains nonmagnetic Eu^{3+}, but substoichiometric EuN has Eu in a mix of 2+ and 3+ charge states. We show that at Eu^{2+} concentrations near 15%–20% EuN is ferromagnetic with a Curie temperature as high as 120 K. The Eu^{3+} polarization follows that of the Eu^{2+}, confirming that the ferromagnetism is intrinsic to the EuN which is, thus, a novel diluted magnetic semiconductor. Transport measurements shed light on the likely exchange mechanisms.

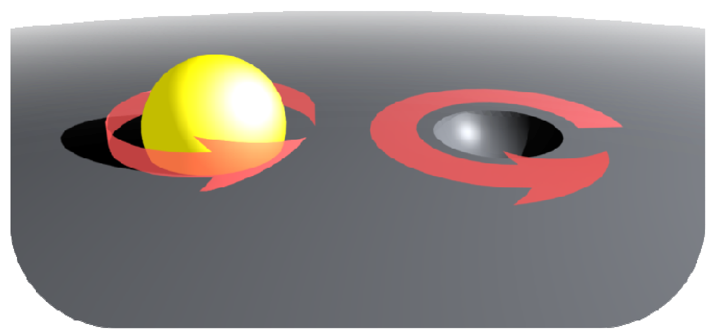
DOI: 10.1103/PhysRevLett.111.167206 PACS numbers: 75.25.−j, 75.47.−m, 75.50.Pp

Applications /Speculation

The holes and electrons have a common (majority) spin.

<u>GdN band structure</u>





Red-majority spin
Blue dashed-minority spin

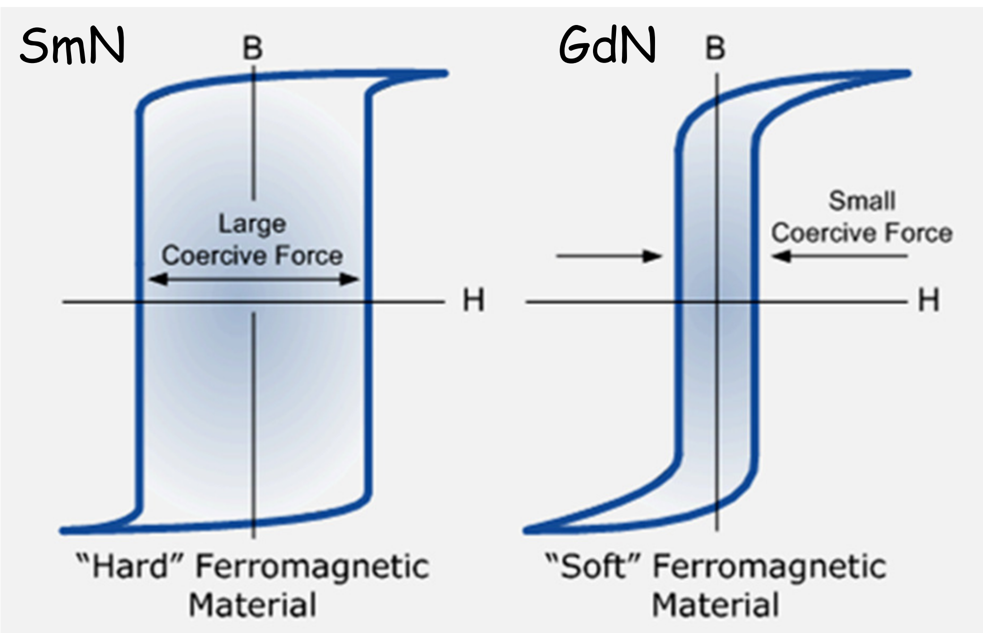
Is it possible to exploit that in spin-resolved electronic devices?

Trodahl *et al.*, Phys Rev. B 76, 085211 (2007)

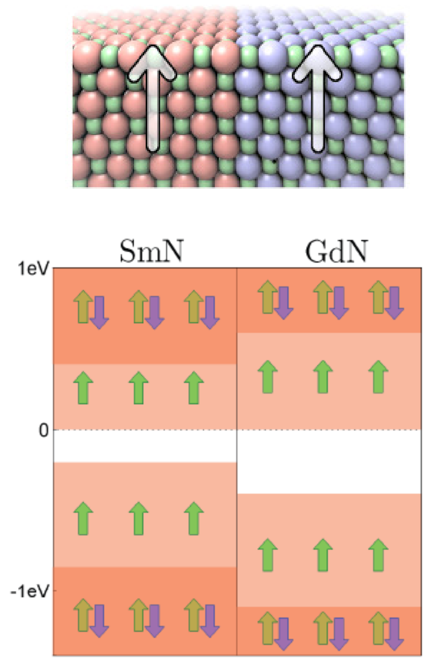
GdN/SmN superlattice for MRAM applications?

Based on the huge coercive-field contrast between SmN (>6T) and GdN (<0.5T)

Switching of a SmN/GdN MRAM expected to be eased by the 10^3 contrast of their coercive fields.

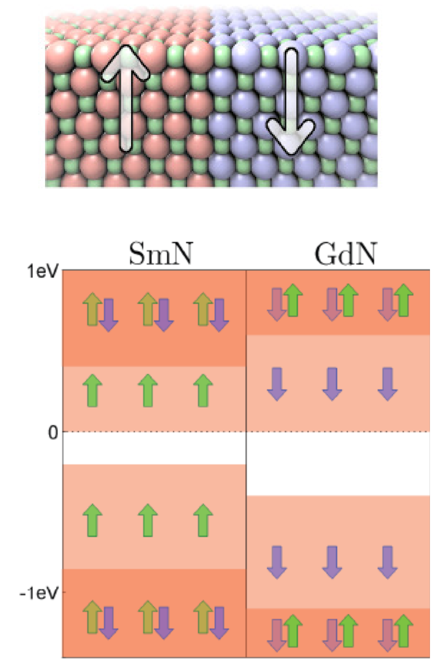


SmN GdN



Low resistance
parallel **M**

SmN GdN



High resistance
antiparallel **M**

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B. Ruck, J. Trodahl, E. Anton, B. Le Do, H. Warring, T. Maity, J. McNulty, L. Figueras, S. Granville.

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S. Vézian, B. Damilano, F. Semond (CRHEA/CNRS, Valbonne), C. Meyer (Institut Neel/CNRS, Grenoble), W. Lambrecht (Case Western Reserve University)..

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Marsden grant (2014-2017) : "Semiconductor-based spintronics: can rare-earth nitrides and group III-nitrides get it together?"

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