Influence of Fermi-level on the lattice location of ^{27}Mg in GaN

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(Emission Channeling with Short-Lived Isotopes, the EC-SLI collaboration)

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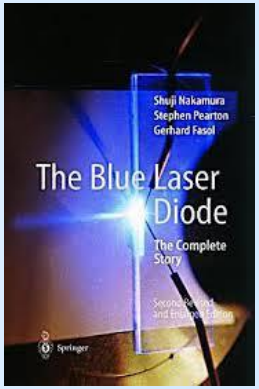
Motivation: Mg in nitride semiconductors

Nobel prize in Physics 2014
I. Akasaki,
H. Amano,
S. Nakamura

- **Nitrides are base material e.g. for white LEDs, blue lasers, power devices, voltage transformers**



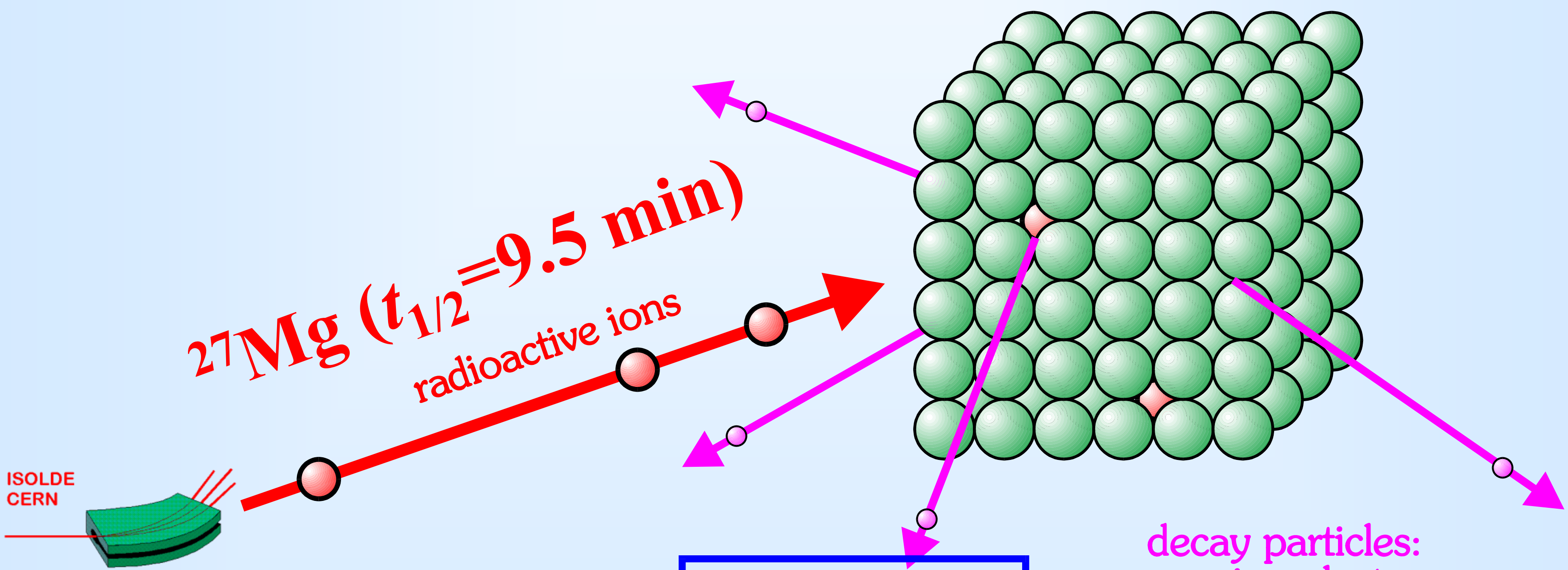
- **Mg is the only technologically relevant *p*-type dopant in GaN**

- **To be electrically active, Mg acceptors (group II) should occupy substitutional Ga (group III) sites**

- **However, if [Mg] > 10^{20} cm^{-3}, Mg becomes inactive**

- **Emission channeling experiments at ISOLDE were the first to reveal also interstitial Mg sites**

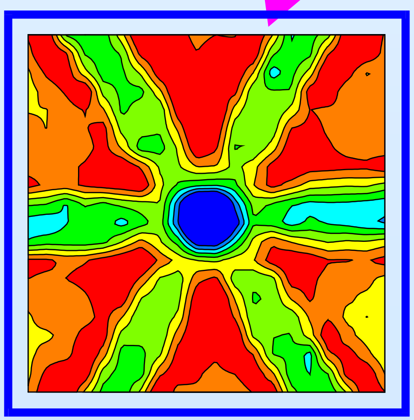
Emission channeling: basic principle



decay particles:
conversion electrons,
β^-, β^+, α

3×3 cm^2 Si pad detector
22×22 pixels of 1.3×1.3 mm^2
currently: max. ~ 5 kHz

2-dimensional
position- and energy-
sensitive detector



2D emission patterns
characterize
specific lattice sites
of the emitting atoms

Direct evidence for amphoteric nature of Mg in GaN

2016 results

PRL **118,** 095501 (2017) PHYSICAL REVIEW LETTERS week ending 3 MARCH 2017

Lattice Location of Mg in GaN: A Fresh Look at Doping Limitations

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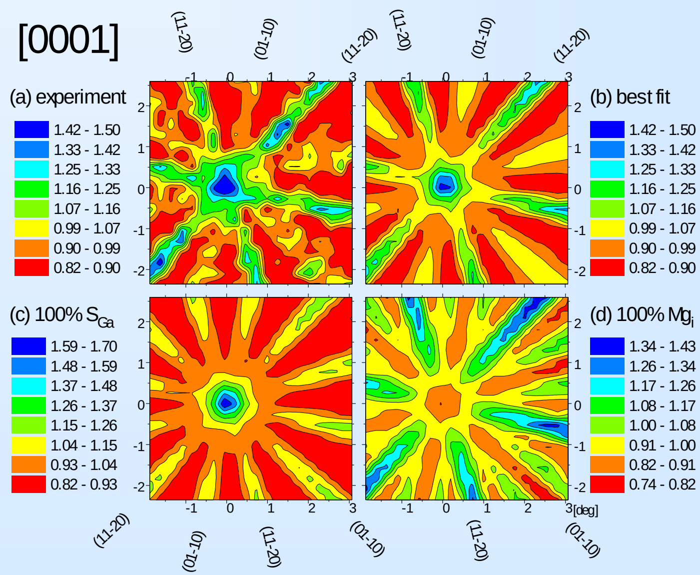
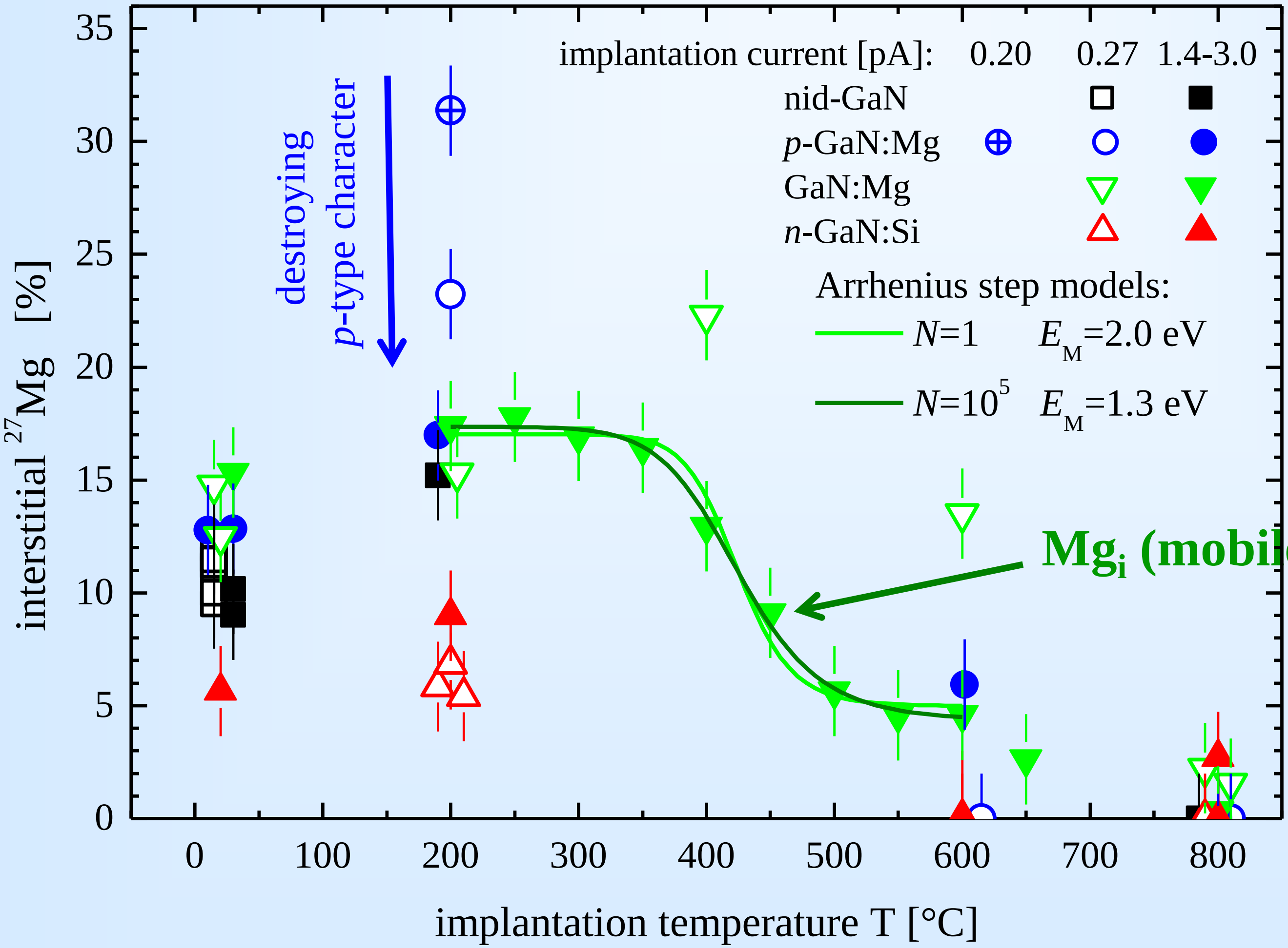
- **[0001] emission channeling patterns quantify implanted interstitial $^{27}Mg_i$ with accuracy of a few %**
- **^{27}Mg EC pattern in *p*-GaN:Mg at RT: superposition of 72% substitutional, 31% interstitial**
- **Studied 4 GaN doping types:**

  undoped GaN
  ***n*-GaN:Si with [Si]=10^{19} cm^{-3}**
  ***p*-GaN:Mg with [Mg]=2×10^{19} cm^{-3} 800°C annealed**
  GaN:Mg with [Mg]=2×10^{19} cm^{-3} as grown



Interstitial ^{27}Mg in different doping types of GaN

2016 results



1 beam spot per sample

Mg_i (mobile) + V_{Ga} → Mg_{Ga}

$f_i = f_{i0}\, N\, \nu_0 \tau \exp[-E_M/k_B T]$

with attempt frequency

$\nu_0 = 2\times10^{13}\ s^{-1}$

- **Interstitial Mg_i enhanced in *p*-GaN and suppressed in *n*-GaN.**
- **Site change of ^{27}Mg from interstitial to substitutional Ga sites as function of implantation temperature allows to estimate activation energy for migration of Mg_i as $E_M \approx 1.3–2.0$ eV.**

U. Wahl et al, PRL 118 (2017) 095501

EC-SLI results are being compared to theory already

- **Recent theory paper on light group I and II elements in Ga**

Phys. Status Solidi RRL **11**, No. 7, 1700081 (2017) / **DOI** 10.1002/pssr.201700081

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Migration of Mg and other interstitial metal dopants in GaN

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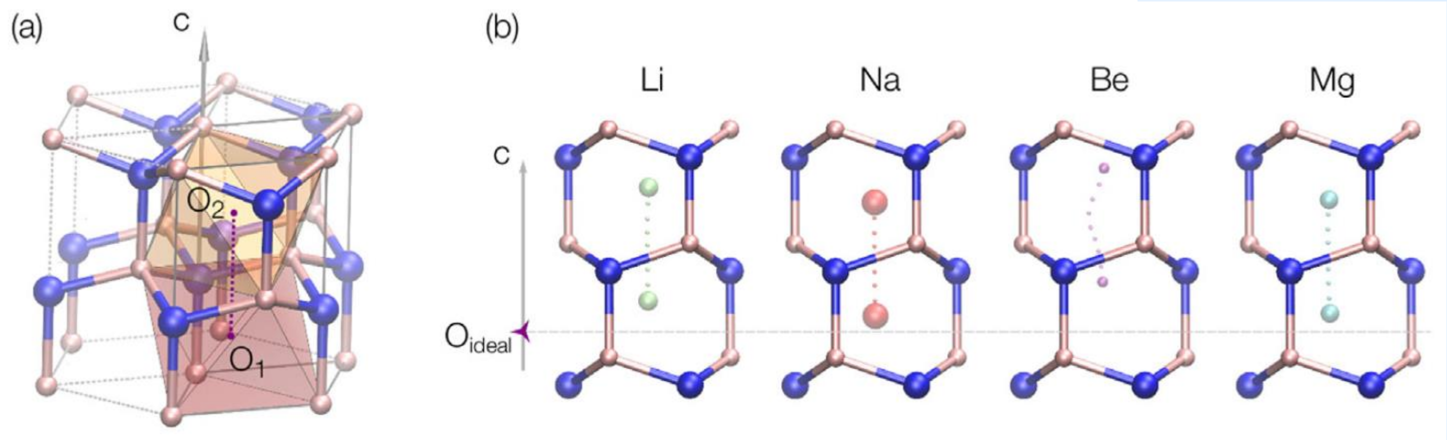
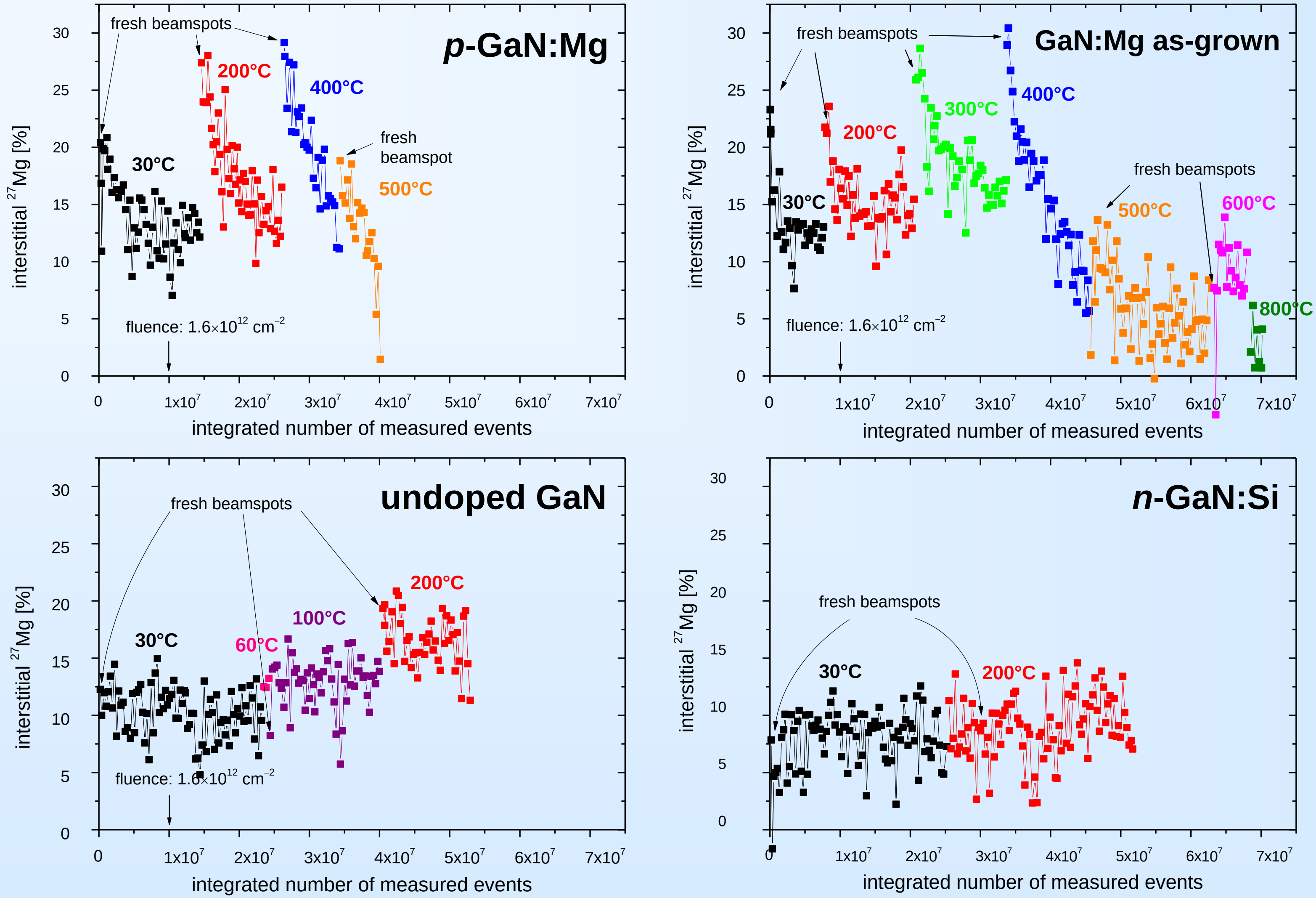
Table 2 Energy barriers (in eV) for the migration of Li^+, Na^+, Be^{2+}, and Mg^{2+} along three different diffusion paths.

cation	path *c*	path *a*	path *b*
Li^+	1.05	1.16	–
Na^+	2.41	2.95	2.01
Be^{2+}	1.88	0.76	–
Mg^{2+}	2.01	2.20	2.19



- **Predicted Mg_i site diverts somewhat (0.6 Å) from EC-SLI position**
- **Calculated migration energy (2.01-2.20 eV) at upper end of estimates from EC-SLI (1.3-2.0 eV)**

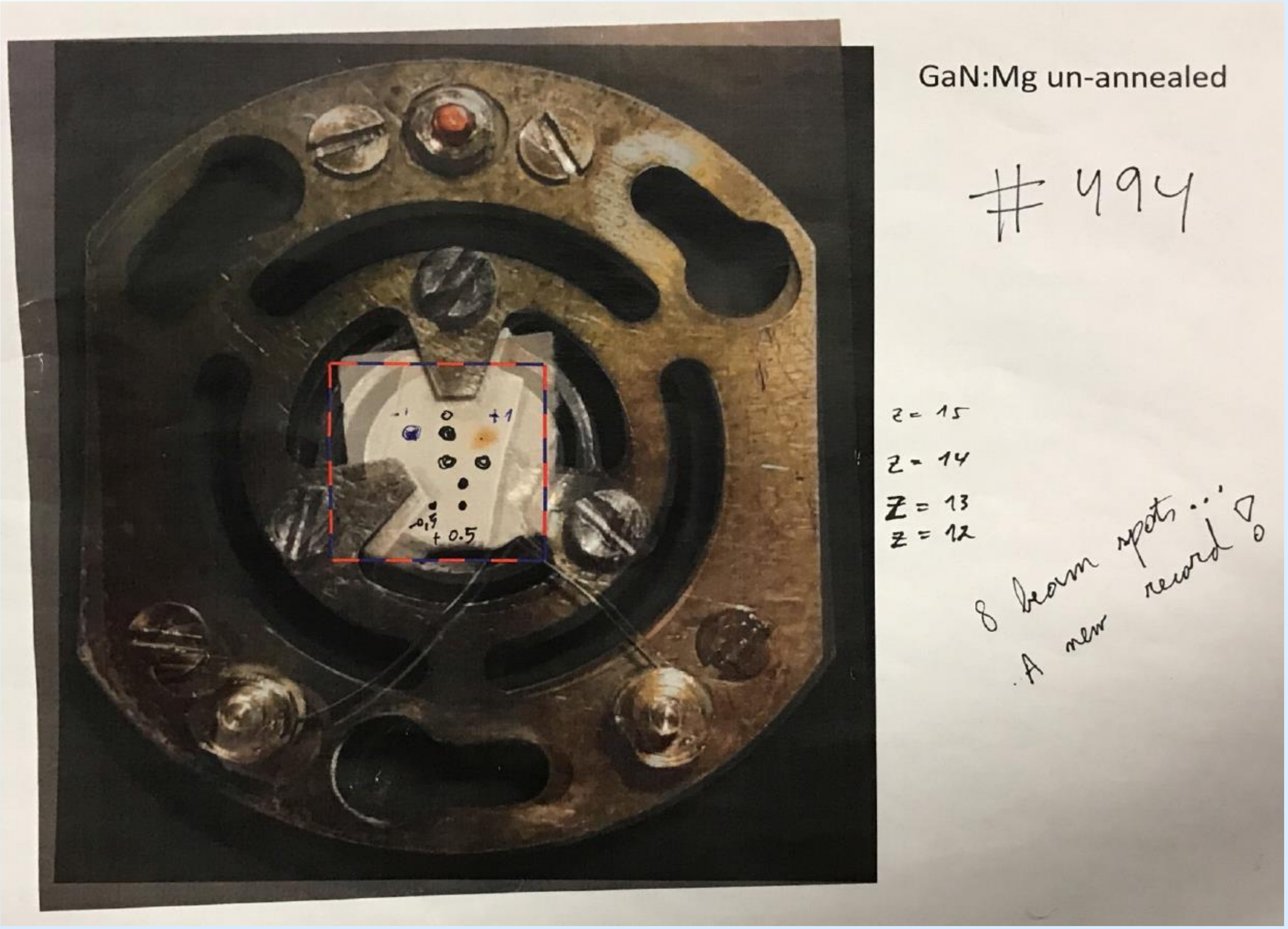
Fluence dependence of interstitial ^{27}Mg in different GaN doping types



2017 results

- **Interstitial Mg_i enhanced in *p*-GaN and suppressed in *n*-GaN**
- **Increase of implantation damage ⇒ interstitial fraction in Mg-doped GaN reaches same levels as in undoped GaN, ~4× faster in GaN:Mg than in *p*-GaN:Mg**

Fluence dependence of interstitial ^{27}Mg in different GaN doping types

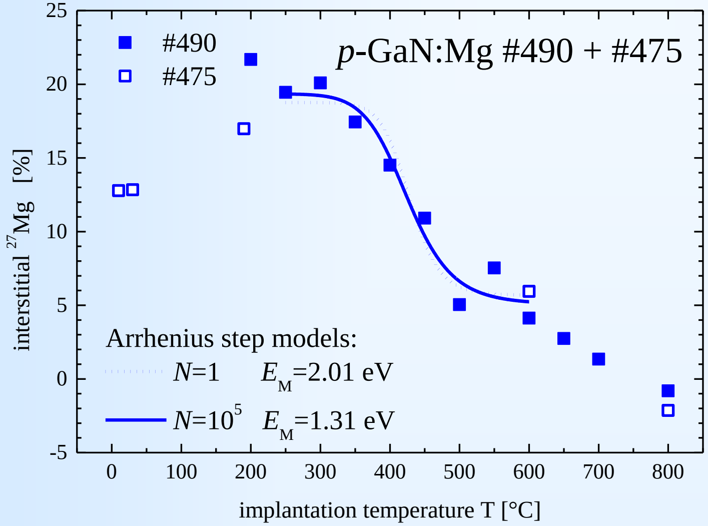


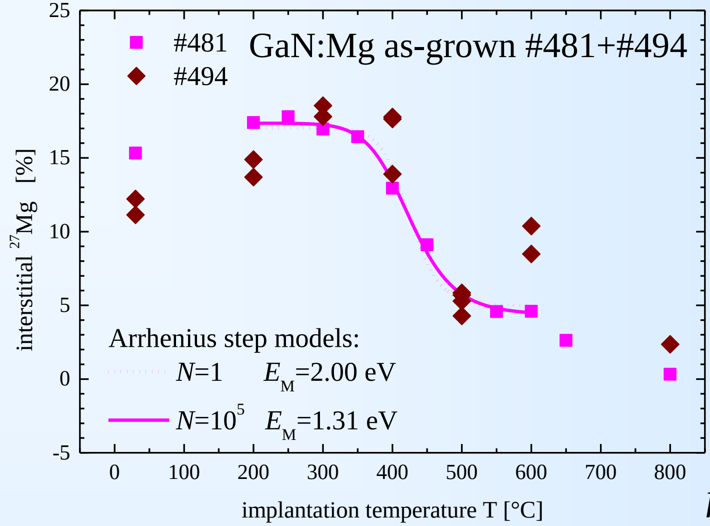
2017 results

up to 7 beam spots per sample!

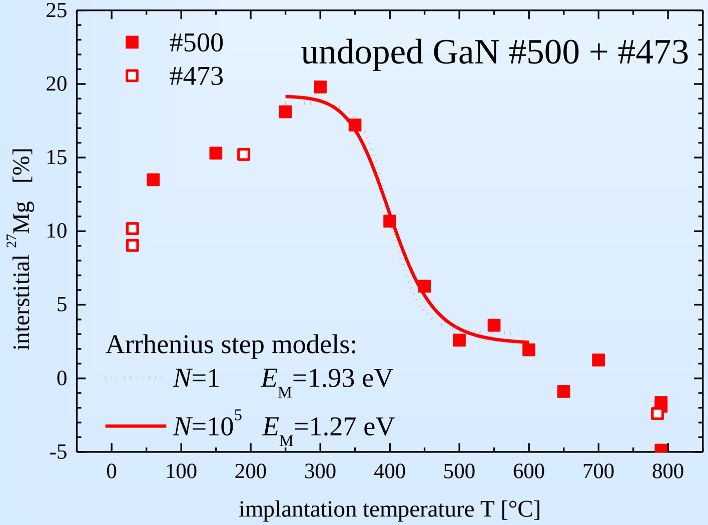
Site change $^{27}Mg_i \rightarrow {}^{27}Mg_{Ga}$ in different GaN doping types: Arrhenius curves

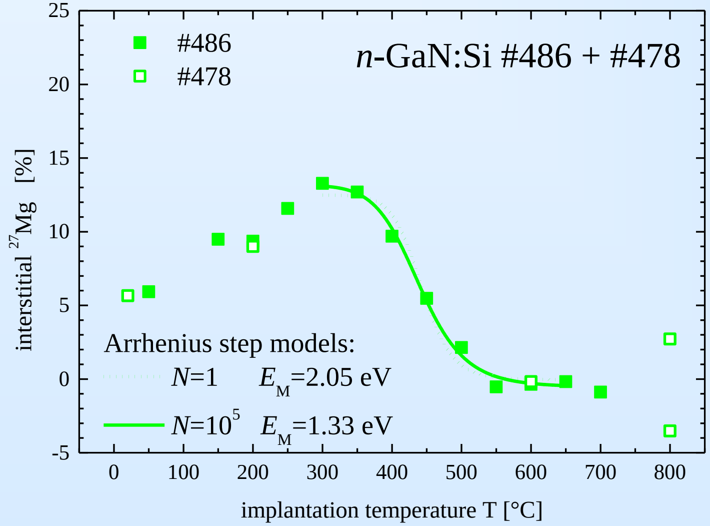
2017 results





$f_i = f_{i0}\, N\, \nu_0 \tau \exp[-E_M/k_B T]$
with attempt frequency
$\nu_0 = 2\times10^{13}\ s^{-1}$

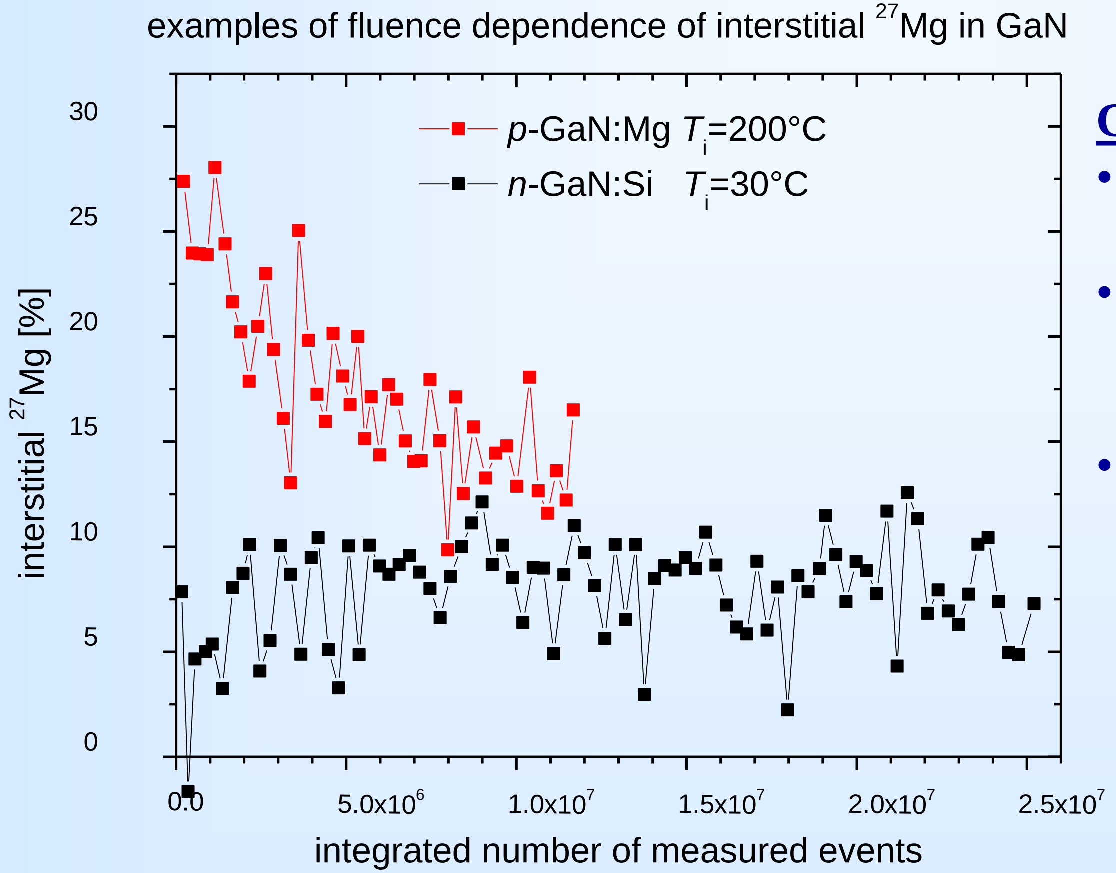




- **Estimated activation energy for migration of Mg_i in all doping types $E_M \approx 1.27–2.01$ eV.**
- **Number of jumps $N=10^5$ $E_M \approx 1.3$ eV always fits a bit better…**

Non-statistical fluctuations of Mg_i fractions

2017 results



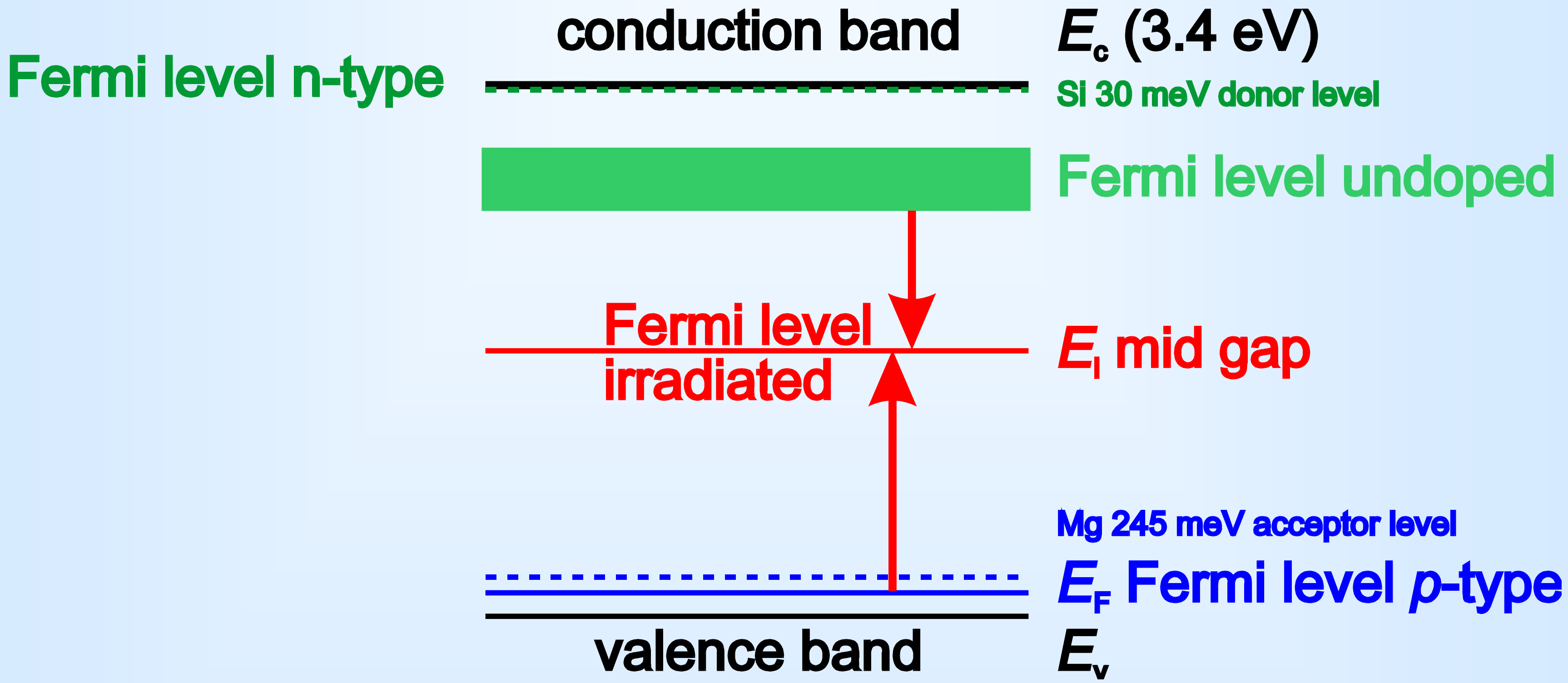
<u>Charging up</u> caused by:

- **implantation current (~0.2-3 pA)**
- **emission of secondary electrons (~3.5 e^- per implanted ion)**
- **outgoing β^- particles**

• "Strange" variations in interstitial Mg_i fractions, e.g. transients, quasi-periodical drops of >5% etc, cannot be explained by statistical fluctuations (should be ~±1%)

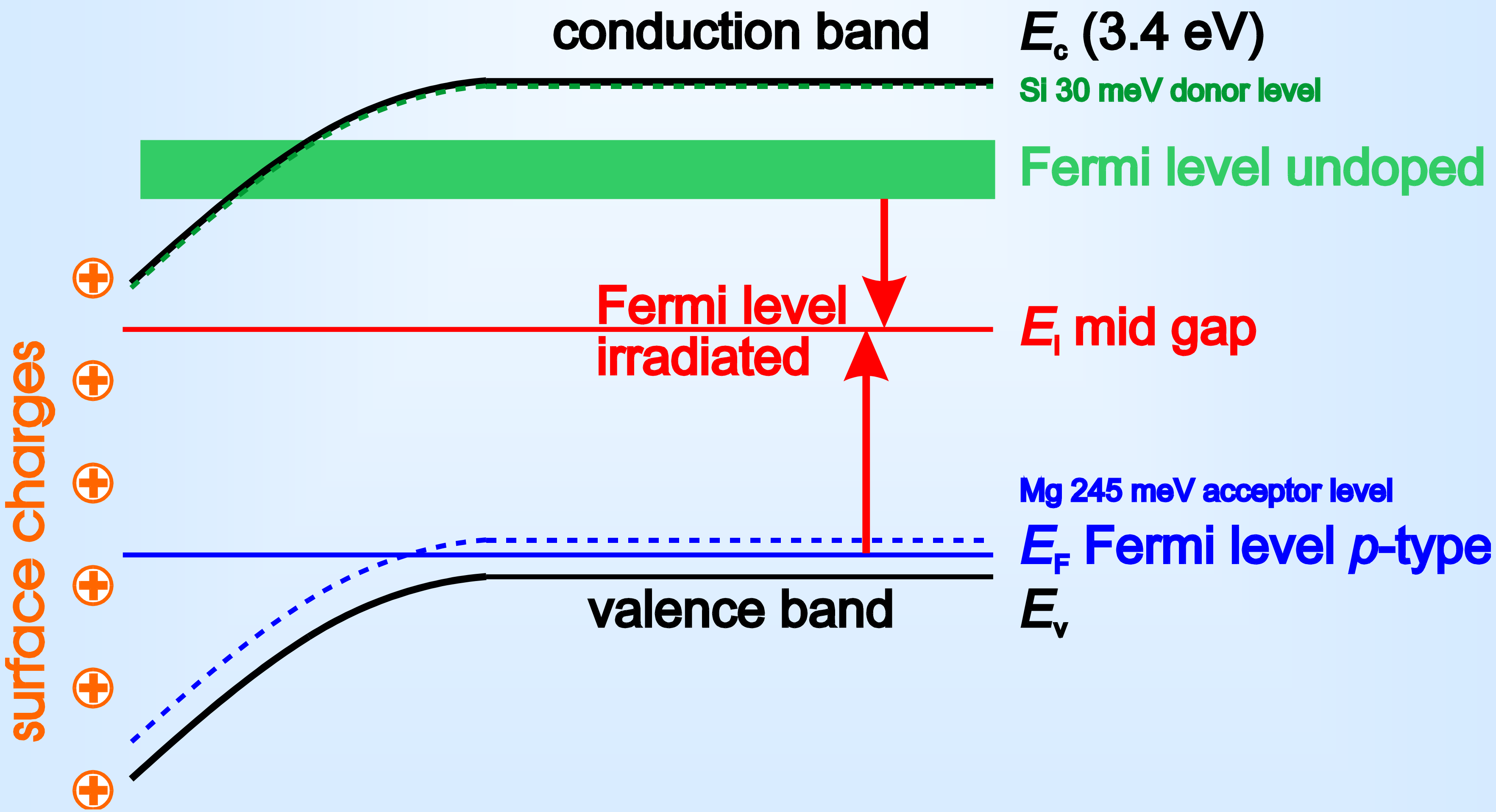
• Our explanation: positive <u>charging up</u> of the surface of the GaN sample (GaN thin film deposited on sapphire, a very good insulator)

Fermi level dependence of Mg lattice site



- Interstitial Mg_i is most abundant when Fermi level is close to valence band
- Pushing the Fermi level towards mid gap (deep levels resulting from radiation damage) reduces interstitial Mg_i
- Fermi level close to conduction band gives lowest fractions of interstitial Mg_i

Fermi level dependence of Mg lattice site



- Build up of positive surface charges bends the band edges downwards while Fermi level stays constant
- ^{27}Mg probes located in the region of the band bending experience a Fermi level closer to mid gap, hence $^{27}Mg_i$ interstitial fraction is reduced

^{11}Be in GaN: a similar case? !

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Amphoteric Be in GaN: Experimental Evidence for Switching between Substitutional and Interstitial Lattice Sites

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(Received 28 June 2017; published 9 November 2017)

We show that Be exhibits amphoteric behavior in GaN, involving switching between substitutional and interstitial positions in the lattice. This behavior is observed through the dominance of Be_{Ga} in the positron annihilation signals in Be-doped GaN, while the emergence of V_{Ga} at high temperatures is a consequence of the Be impurities being driven to interstitial positions. The similarity of this behavior to that found for Na and Li in ZnO suggests that this could be a universal property of light dopants substituting for heavy cations in compound semiconductors.

DOI: 10.1103/PhysRevLett.119.196404

- **Clearly an interest in lattice location studies also for Be**

- **We have already proof of existence of interstitial $^{11}Be_i$ at positions (–0.66±0.13) Å from O sites (parasitic experiments in 2012).**

- **Only RT measured so far. higher temperatures needed for site change $Be_i \rightarrow Be_{Ga}$ resulting from migration of Be_i. Theoretical predictions: E_M=1.2-2.9 eV [Van de Walle PRB 2001], E_M=0.76-1.88 eV [Miceli PSSRRL 2017].**

- **Looking forward to approved experiments with ^{11}Be to be scheduled in 2018.**

Conclusions

- **2017: full confirmation of amphoteric nature of Mg in GaN**
- **Interstitial *vs* substitutional Mg fractions depend on**
  - **Doping type: up to ~30% interstitial Mg_i found in *p*-GaN, <10% in *n*-GaN**
  - **Radiation damage: pushes Mg_i fractions towards situation in undoped GaN**
  - **Temperature: site change of mobile $Mg_i \rightarrow Mg_{Ga}$ at 400°C and above**
  - **Possible influence of surface charges**

- **Results can be explained based on a Fermi level model**

- **Looking forward to approved experiments with ^{11}Be in 2018**

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